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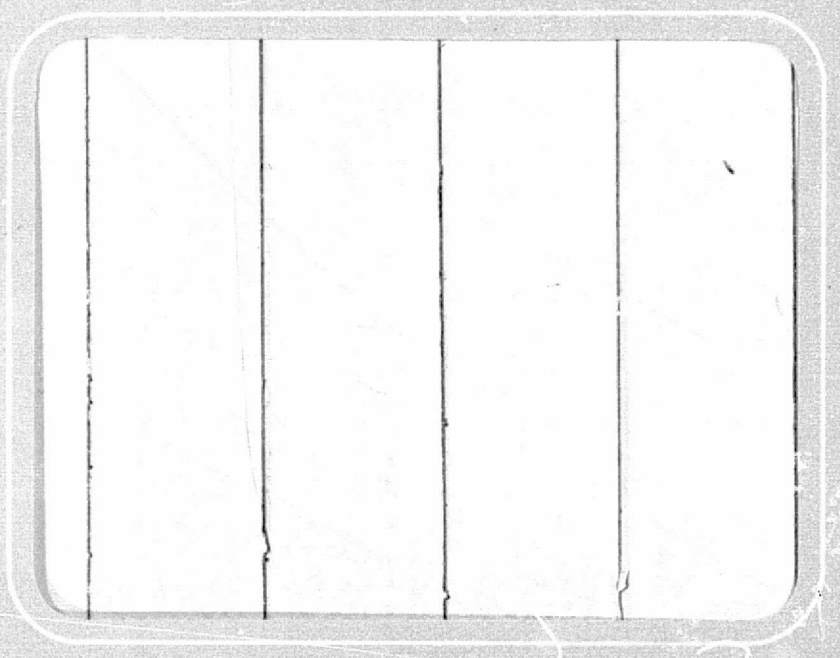
Report



TECHNICAL REPORT

on

QUANTUM CHEMICAL CALCULATIONS OF INTERATOMIC POTENTIALS FOR COMPUTER SIMULATION OF SOLIDS

NSG-2027

to

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Ames Research Center

September 30, 1977

BATTELLE
Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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I. INTRODUCTION

The basic factors controlling the strength of materials are found at the atomic scale of material structures. The availability of this type of structural detail is essential to the interpretation of available experimental data. It lies at the heart of our ability to predict and modify the strength of materials to suit our technological needs. Unfortunately, the direct experimental observation of the atomic scale phenomena determining the strength of metals has proven impossible; other approaches are needed in order to obtain the atomic scale picture. We at Battelle have developed a comprehensive mathematical model by which the collective behavior of a very large number of atoms within a metal or alloy can be accurately simulated[1]. In particular, the manner in which the atomic interactions relate to dislocation motion and crack extension to determine the strength of a metal can now be determined and dissected by this method. Our current effort is in understanding the factors determining resistance to crack extension in iron metal subject to a stress, and how the presence of hydrogen causes crack extension to proceed at abnormally low stresses.

II. TECHNICAL PROGRESS

A. Overview of the Areas of Current Progress

When this project started its main emphasis was on the calculation of the interatomic forces. This is one of the basic ingredients in the simulation of stress crack extension of metals in the presence of hydrogen. However, in the process of exercising the crack simulation model, even with empirical interatomic forces, it became clear that something was seriously wrong. The effort in the calculation of the interatomic forces was consequently reduced, and attention was focused on identifying the source of the problem in the crack simulation model. The material in this report thus reflects the spread of the effort to both complementary aspects of the project. The material is presented in the following order.

- Brief sketch of the problems encountered with Gehlen's crack simulation model
- Identification of the source of error in the crack simulation model
- New improved formulation of the crack simulation model
- Electronic structure calculation of small iron atom clusters, their stability as a function of configuration, and the effect of adding a hydrogen atom.

B. Sketch of the Problems

The basic crack simulation model with which we have been working is that pioneered by P. C. Gehlen at the Battelle Columbus Laboratories. In order to place the magnitude of the difficulties with the model in perspective it is necessary to present first some background information. The physical problem being studied is the resistance to crack extension which arises from the lattice structure in metals. This resistance to crack extension is shown in Figure 1 in the form of the energy barrier

(at a fixed stress intensity) between any two adjacent equilibrium crack positions

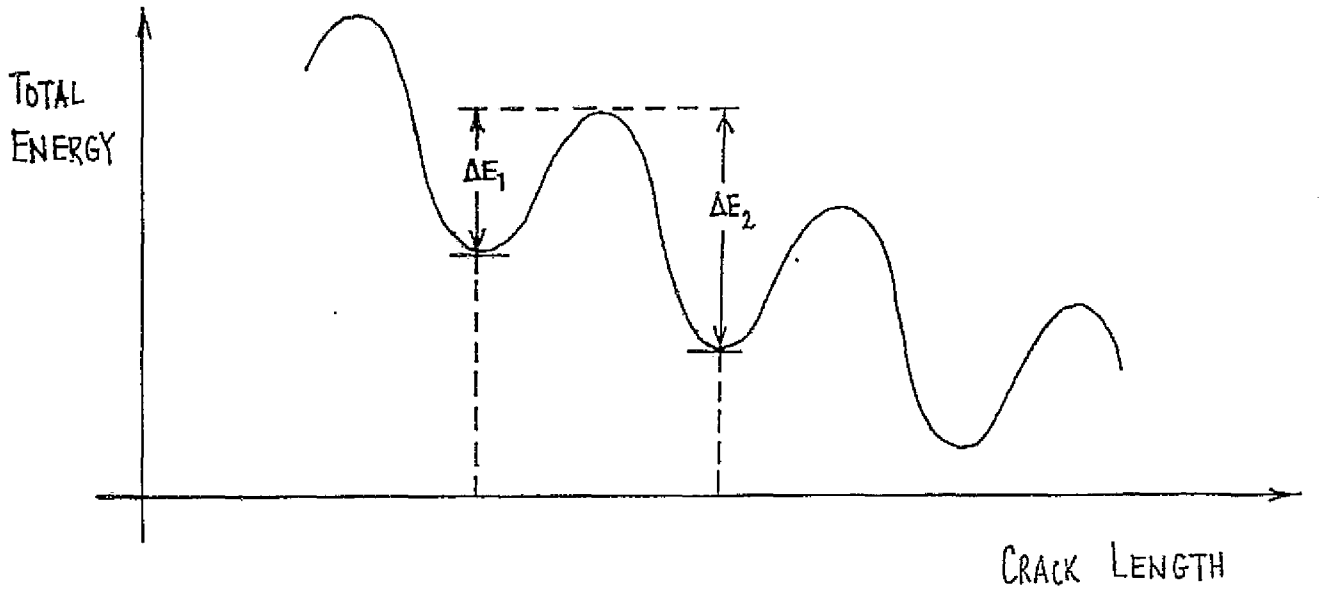


FIGURE 1.

If one obtains the ΔE_1 and ΔE_2 energy barriers (barriers to crack extension and healing respectively) at various stress intensities, K, one expects a behavior illustrated in Figure 2.

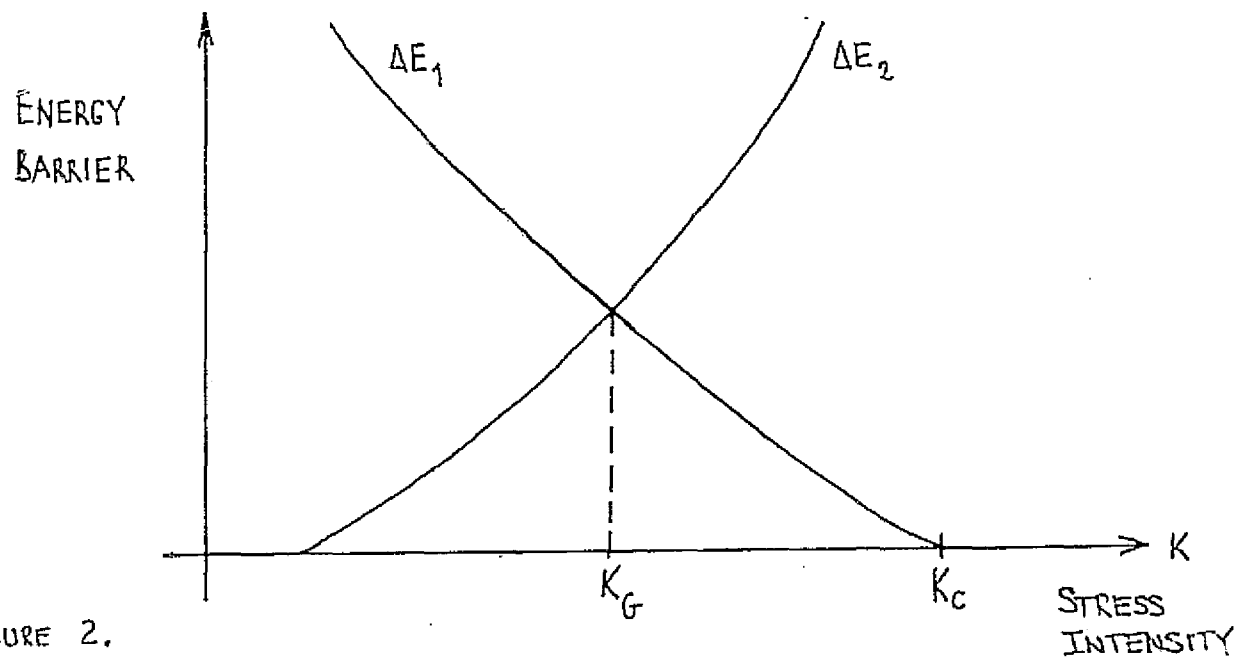


FIGURE 2.

The ΔE_1 and ΔE_2 curves cross at what is called the Griffith stress intensity[2]. At this point the rate of continuum strain energy release equals the rate of surface energy, γ, creation

$$\frac{K^2}{E} = 2\gamma \qquad \text{for} \quad K = K_G$$

where E is Young's modulus. Although from an elasticity-theory point of view cracks become unstable for $K > K_G$, these do not propagate readily because of the "lattice trapping" illustrated in Figure 1 as first pointed out by Hsieh and Thomson[3]. Only for $K = K_C$ does all resistance to crack extension dissappear as the barrier ΔE_1 goes to zero.

Contrary to what one expected, the application of the crack simulation model to this problem predicted that the barrier to crack extension would not disappear. It led to results of the type shown in Figure 3.

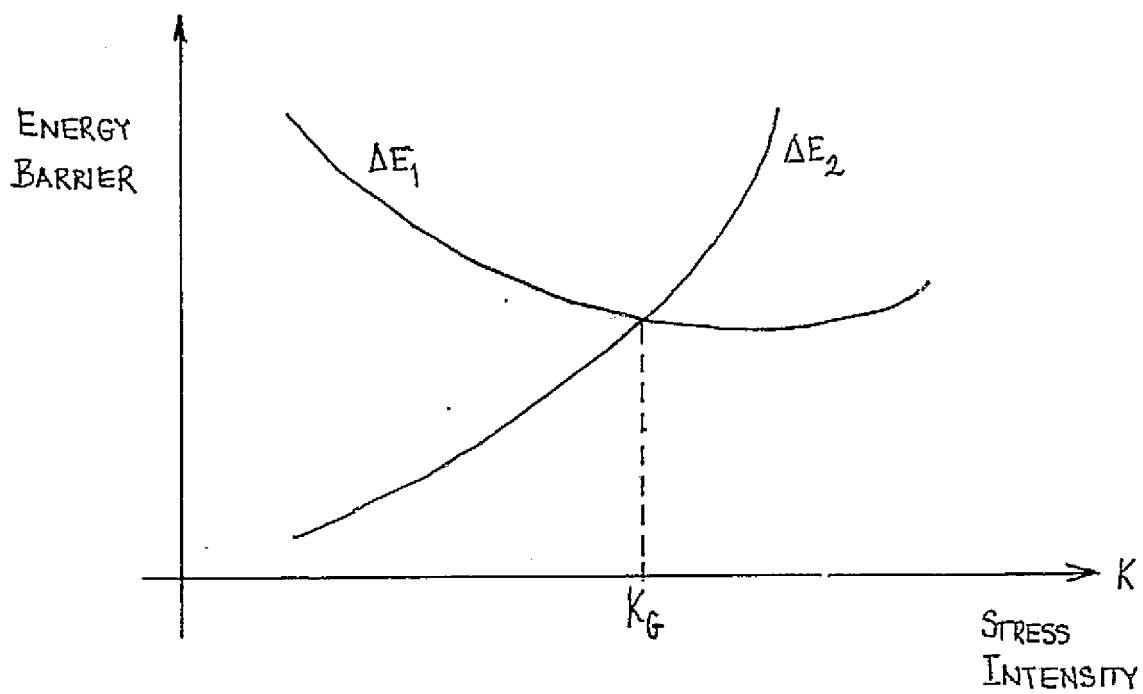


FIGURE 3.

This unphysical result was attributed to the use of a linear elastic field in the description of the continuum region. The latter is the region within

which the discrete crack core region is embedded. Subsequently, a considerable amount of effort was expended in replacing the linear elastic field by a general non-linear field which was based on the use of Green's functions to fold residual forces into modified equilibrium displacement fields[1]. Unfortunately, when the corresponding energy barriers as a function of stress intensity were calculated by this considerably more sophisticated method, they made even less physical sense than those obtained previously.

Furthermore, disturbing convergence to different relative minima were found depending on the procedure used to locate these minima and convergence to the saddle points was plagued with difficulties. The magnitude, persistence, and uncertain origin of these problems, in spite of the constant and well reasoned efforts to overcome them, persuaded P. C. Gehlen, the originator of the simulation model, that the approach lacked validity. He was discouraged from further pursuing the source of the difficulties.

C. Identification and Analysis of the Sources of Error

We have given Gehlen's procedures a detailed examination. This effort has brought to light some fundamental assumptions in his model which are found to be incorrect. The deficiencies in Gehlen's model, in essence, fall into three categories although they are interrelated.

- Disregistry between the continuum and discrete region crack fields
- Neglect of the contribution of the continuum strain energy release
- Inconsistent definition of potential energy and gradients thereof

We shall discuss each of these points next.

1. Disregistry Between the Continuum and Discrete Region Crack Fields

We found that in the simple rigid boundary model, apart from restricting the elastic crack field to be linear, the origin of the field was always held fixed at an arbitrary position. Thus, even when the discrete region would describe an advanced crack, e.g. saddle point or an adjacent stable crack, the field describing the continuum would still be

fixed in its arbitrary original position. We refer to this as the disregistry effect arising from the incorrect relative alignment of the fields in both discrete and continuum regions. This is depicted schematically in Figure 4.

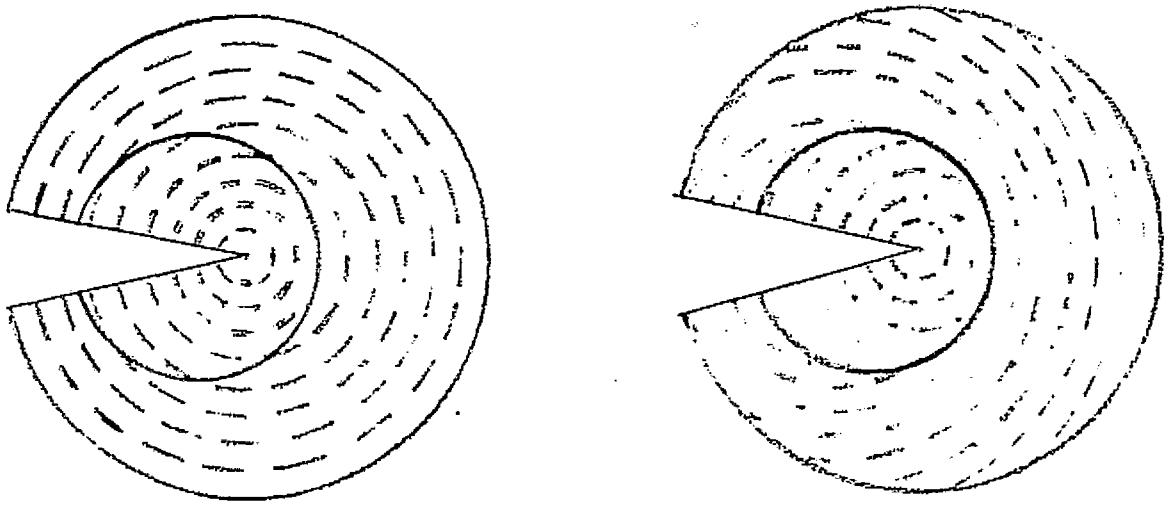


FIGURE 4.

It was found that when the disregistry was minimized by advancing the elastic fields together with the discrete region, the relative stability of two adjacent equilibrium cracks changed by amounts of the same magnitude as those of the energy barriers we were looking for. Thus, the disregistry effect was found to be an important source of the errors in the results shown in Figure 3. The introduction of the flexible boundary model in principle solves this problem. It is designed to fully relax the continuum region, i.e. to both introduce non-linear effects and to minimize the disregistry effect. In practice the relaxation of this elastic field was not direct, but entered only as a response to a separate

full relaxation of the atoms in the discrete region. The latter region was relaxed by the "kinetic energy quenching" method[4]. There remains in practice the possibility that, as the kinetic energy is quenched in the discrete region, the rate at which information about disequilibrium is transferred to the continuum region becomes exceedingly small. This would result in only a partly minimized disregistry effect. This however, was probably only a minor error in the flexible boundary model. The major reason why this improved model failed was an imcomplete accounting of the terms in the total energy of the system. This is discussed in the next subsection.

Before going on it is worth noting aspects of the saddle point calculations which were affected by the disregistry. In the rigid boundary model, the same type of disregistry error was introduced as in searching for equilibrium minimum positions. In the flexible boundary case, the continuum atoms were left positioned at the maximum of the energy along a straight line interpolating from their position in the two equilibrium cracks on either side of the saddle point. Although the continuum was not further relaxed in searching for the saddle point, this is probably by itself only a minor effect. The major error in the saddle point calculation arises from the calculation of forces on the atoms by a formula which is inconsistent with the definition of the potential energy of the model. This will be discussed in the third subsection.

2. Neglect of the Energy Exchange With the Continuum

When the elastic field of the continuum region advances in order to minimize the disregistry effect with the discrete region, then, from elasticity theory, one can calculate the strain energy released from the continuum which flows into the crack tip region as depected schematically in Figure 5.

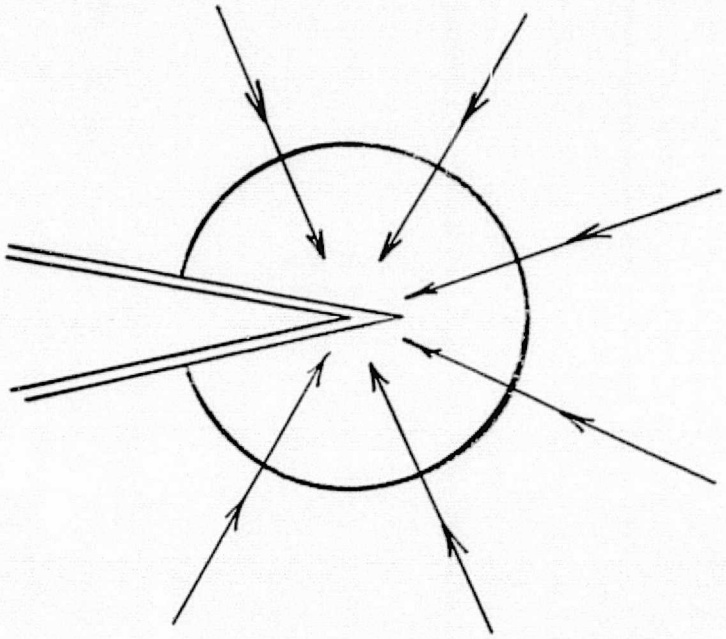


FIGURE 5.

This strain energy release[2] is given by

$$\frac{K^2}{E} a \Delta b$$

where K is the stress intensity, E is Young's modulus, Δb is the advance of the crack elastic field, and "a" stands for the thickness of the slices in the model. This energy change of the continuum has to be combined with the energy change of the discrete region. These two energy changes are shown in Figure 6.

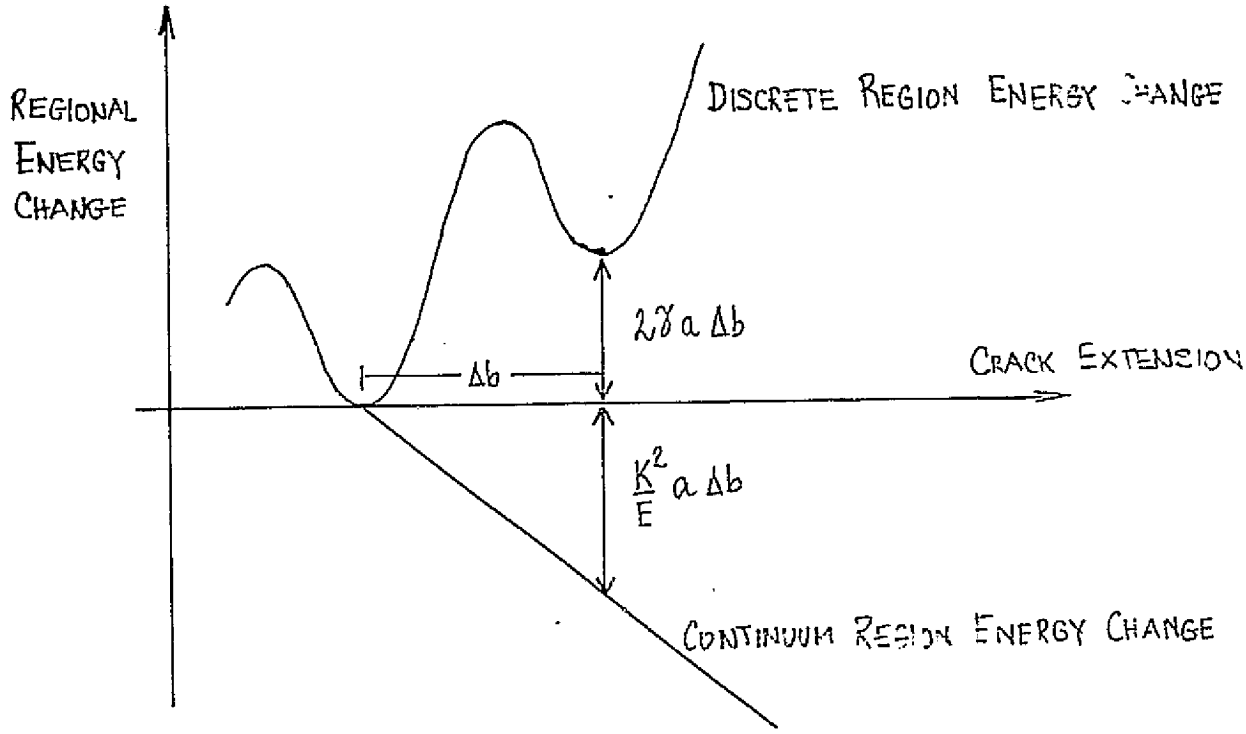


FIGURE 6.

The energy change of the discrete region is typical of calculations where the disregistry effect has been minimized by advancing the continuum together with the discrete region crack. At a repeat distance Δb one finds that this energy has increased (within the accuracy of the model) by the surface energy created, i.e. $2\gamma a \Delta b$, where "a" stands for the width of the main slice in the model. The combined energy change is shown in Figure 7 for the case when crack growth is favored.

$$\frac{K^2}{E} > 2\gamma = \frac{K_G^2}{E}$$

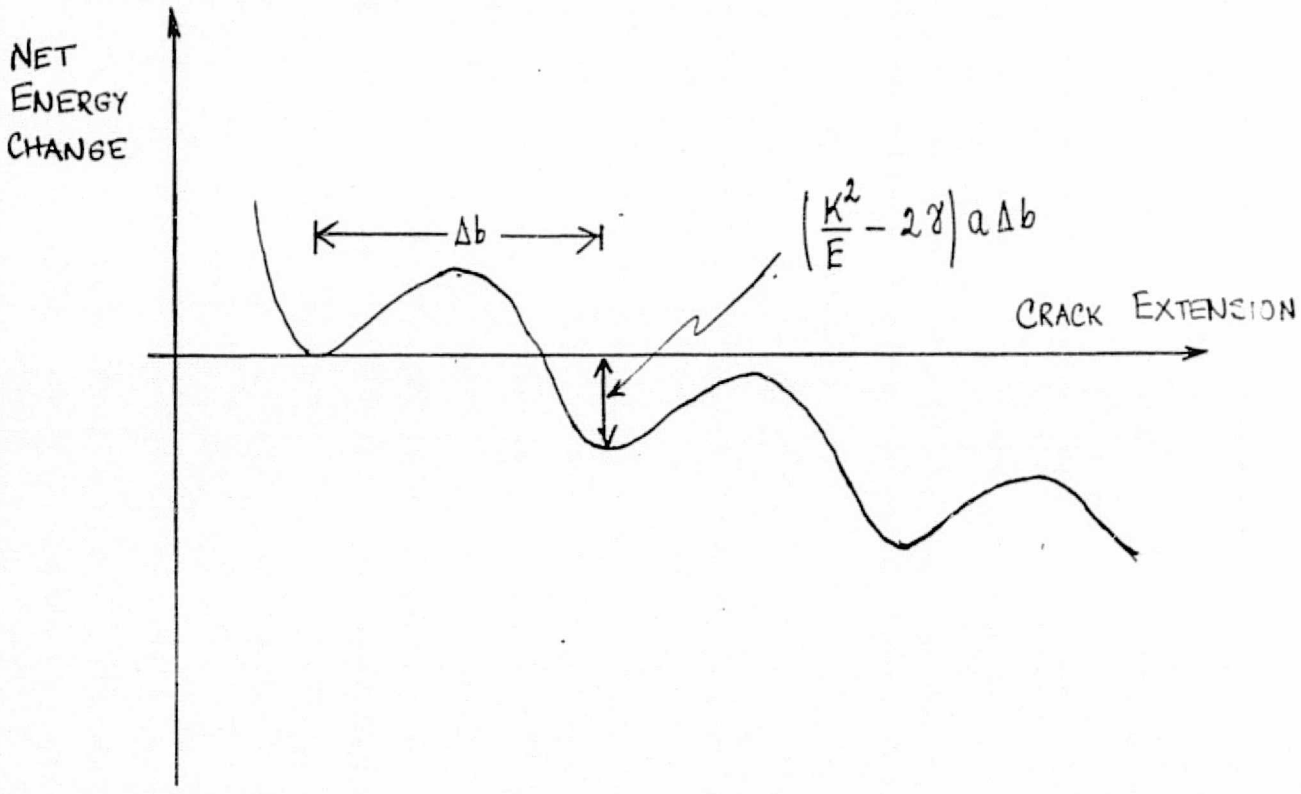
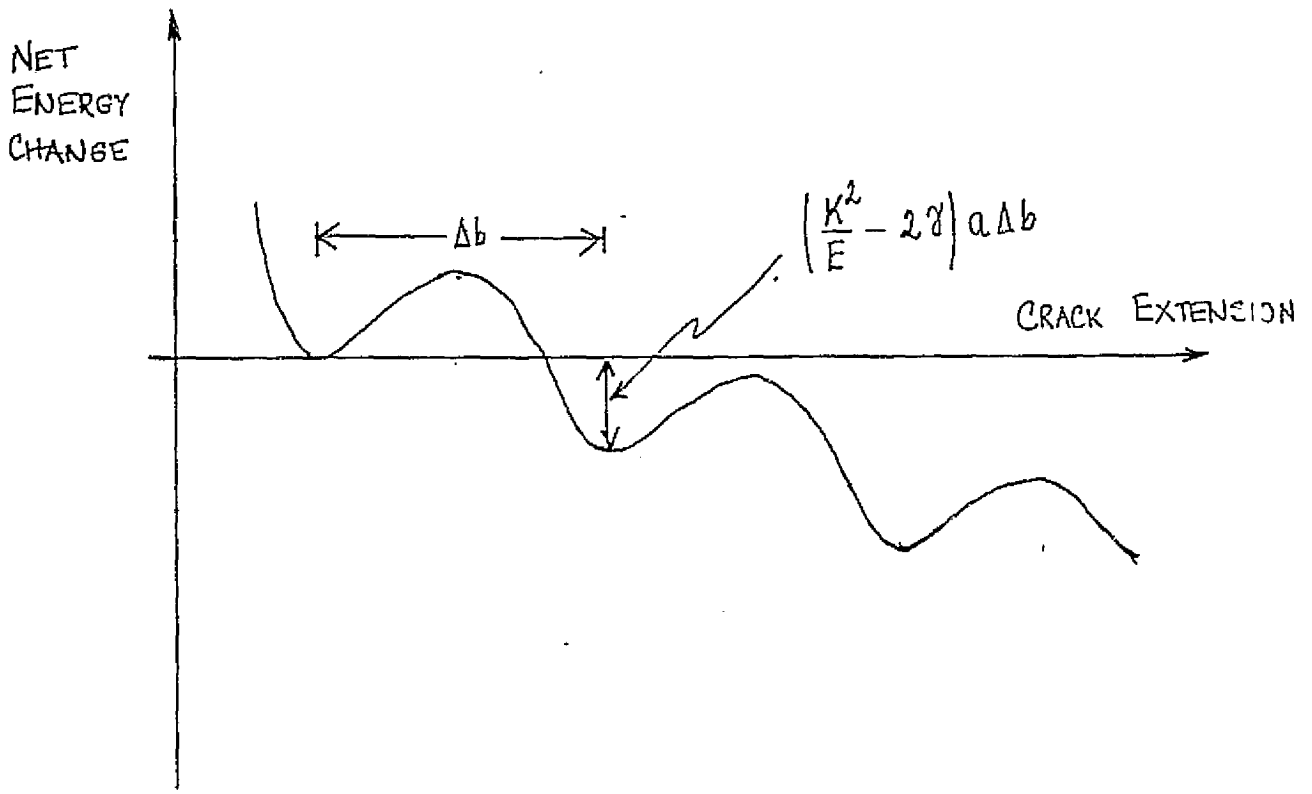


FIGURE 7.

In Gehlen's rigid boundary model the disregistry effect originating from not allowing the continuum field to advance resulted in an artifactually zero continuum strain energy release. The combined consequence of these restrictions is the underestimation of the basic driving force behind the disappearance of the effective energy barrier to crack extension, as is seen from Figure 7. This explains why the results of Gehlen's rigid boundary calculations shown in Figure 3 predicted that the barrier to crack extension would not disappear. In Gehlen's flexible boundary model the disregistry effect was removed by allowing the field to readjust. The calculation of the strain energy changes associated with these continuum readjustments should provide the required driving force lacking previously.



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We found, however, that these continuum energy changes were unfortunately not included in Gehlen's calculations. The omission of this major energy contribution in both the crack calculations of minima and saddle points is probably the principal reason for the unphysical nature of the results obtained from the flexible boundary model.

3. Inconsistent Definition of Energy and Gradients of the Energy

The forces on each of the atoms are the central ingredient in the search and location of the equilibrium crack minima and saddle points. The definition of the force on the k-th atom used in Gehlen's model is*

$$\underset{\sim}{F}_k^{(1)} = -\sum_{\ell \in B} \nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) - \sum_{\ell \in b} \nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right)$$

This is also the definition which makes most physical sense. The potential energy in Gehlen's model is defined in turn as

$$E^{(1)} = \frac{1}{2} \sum_{k \in B} \sum_{\ell \in B} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) + \frac{1}{2} \sum_{k \in B} \sum_{\ell \in b} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right)$$

containing half of the interaction energy with the continuum. The objective definition of the force on an atom is the negative gradient of the potential energy. Thus, the definition of the model potential energy fixes the definition of the force. In this case we find

$$\underset{\sim}{F}_k^{(2)} = -\nabla_k E^{(1)} = -\sum_{\ell \in B} \nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) - \frac{1}{2} \sum_{\ell \in b} \nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right)$$

It is clear that this is not the definition of the force used by Gehlen. It is not the natural definition since it weights the continuum atoms' contributions differently than the discrete region atoms, yet it is the definition which is consistent with the properties of the model as contained in the potential energy. Gehlen's definition of force would be consistent with a potential energy of the form

$$E^{(2)} = \frac{1}{2} \sum_{k \in B} \sum_{\ell \in B} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) + \sum_{k \in B} \sum_{\ell \in b} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right)$$

---

*See Section F, page 22, for definitions of the terms used here.

The use of Gehlen's definition of force, $\underset{\sim}{F}_k^{(1)}$, in the relaxation techniques leads to the minima and saddle points of $E^{(2)}$. If this were also the potential energy used to calculate the associated energy differences, then there would be no inconsistency error. In Gehlen's model, however, $E^{(1)}$ was used in calculating the energy difference. It was found that the equilibrium configurations of $E^{(1)}$ and $E^{(2)}$ could differ significantly. This is thus another major source of error in the simulation model. It permeates all the applications and versions of the simulation model. In a manner, the inconsistency problem arises because not all necessary energy contributions of the model were built into the potential energy. This is just another aspect of the neglect of the energy terms from which we obtain the continuum strain energy release.

4. Acknowledgements

The analysis and identification of the errors discussed in this section are the result of extended discussions by the author with Drs. P. C. Gehlen, G. T. Hahn, R. G. Hoagland, and A. J. Markworth of the Battelle Columbus Laboratories Metal Science Section.

D. Improved Formulation of the Crack Simulation Model

Our analysis of Gehlen's simulation model shows that, apart from the three previously described conceptual errors, the remaining aspects of his model retain their validity. We have built upon Gehlen's approach in formulating an improved simulation model which incorporates the solution to the conceptual errors in the previous model. The details of the new approach are described in the Appendix to this report. The main points are

- The total energy of the system has been formulated precisely with emphasis on including the contribution from atoms in all regions of the model. The result is

$$E = E_1 + \sum_{k \in 6^*} \left(\underset{\sim}{R}_k - \underset{\sim}{R}^\circ_k \right) \cdot \int_0^1 \nabla_k E_2 \left[\underset{\sim}{R}^\circ + \lambda \left(\underset{\sim}{R} - \underset{\sim}{R}^\circ \right) \right] d\lambda + E_2^\circ$$

  The term E_1 is the energy of the discrete region atoms defined as ($\underset{\sim}{T}_n$ is a translation vector; see Appendix)

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- The total energy of the system has been formulated precisely with emphasis on including the contribution from atoms in all regions of the model. The result is

$$E = E_1 + \sum_{k \in G^*} \left(\underset{\sim}{R}_k - \underset{\sim}{R}_k^0 \right) \cdot \int_0^1 \nabla_k E_2 \left[\underset{\sim}{R}^0 + \lambda \left(\underset{\sim}{R} - \underset{\sim}{R}^0 \right) \right] d\lambda + E_2^0$$

  The term E_1 is the energy of the discrete region atoms defined as ($\underset{\sim}{T}_n$ is a translation vector; see Appendix).

$$E_T = \frac{1}{2} \sum_{k \in B} \sum_{\ell \in B} \left[u\left(|R_k - R_\ell|\right) + \sum_{\substack{n=0 \\ n \neq 0}}^{-\infty} u\left(|R_k - R_\ell - T_n|\right) \right]$$

$$+ \sum_{k \in B} \sum_{\ell \in b} \left[u\left(|R_k - R_\ell|\right) + \sum_{\substack{n=0 \\ n \neq 0}}^{-\infty} u\left(|R_k - R_\ell - T_n|\right) \right]$$

The second term is a work energy term giving the energy change of continuum region atoms relative to a reference strained state R^0 with energy E_2^0. This energy is the source of the continuum strain energy release, $K^2 a \Delta b / E$, discussed in subsection 6.2. The gradient of E_2 in the work energy is defined as

$$\nabla_k E_2 = \sum_{\ell \in b} \left[\nabla_k u\left(|R_k - R_\ell|\right) + \sum_{\substack{n=0 \\ n \neq 0}}^{-\infty} \nabla_k u\left(|R_k - R_\ell - T_n|\right) \right]$$

- The formulation of the complete energy of the system allows us to unify the treatment of the discrete and continuum regions in the search for equilibrium. The search for equilibrium becomes a problem of finding the stationary points of this total energy with respect to all the degrees of freedom in the model. The problem of minimizing the disregistry effect becomes simply part of the process of seeking for the lowest total potential energy.
- The application of the "conjugate gradient" technique of Fletcher and Reeves[5] is discussed as a natural approach in light of the function minimization mold into which we have now cast the simulation model.
- The previously used relaxation technique of "kinetic energy quenching" is extended to the direct relaxation of the parameters of the elastic continuum field.
- The forces on the degrees of freedom of the model are found directly from the gradients of the total potential energy definition.

It is worth noting that in the essential aspects this improved formulation brings Gehlen's basic approach closer to that of Sinclair[6]. One remaining difference lies in the now vivid perspective we have on the singular role the present modifications of Gehlen's model have in making this a valid approach.

E. Electronic Structure Calculations of Clusters of Iron Atoms and The Effect of Inserting Hydrogen

Our goal is to obtain detailed information about the interaction of a hydrogen atom with an environment of iron atoms. This is the basic ingredient to the crack simulation of hydrogen-enhanced stress cracking of iron. Our approach is to carry out a series of cluster calculations with a hydrogen atom placed variously within iron atom clusters. An example configuration is that of hydrogen at an octahedral site in bcc iron as shown in Figure 8.

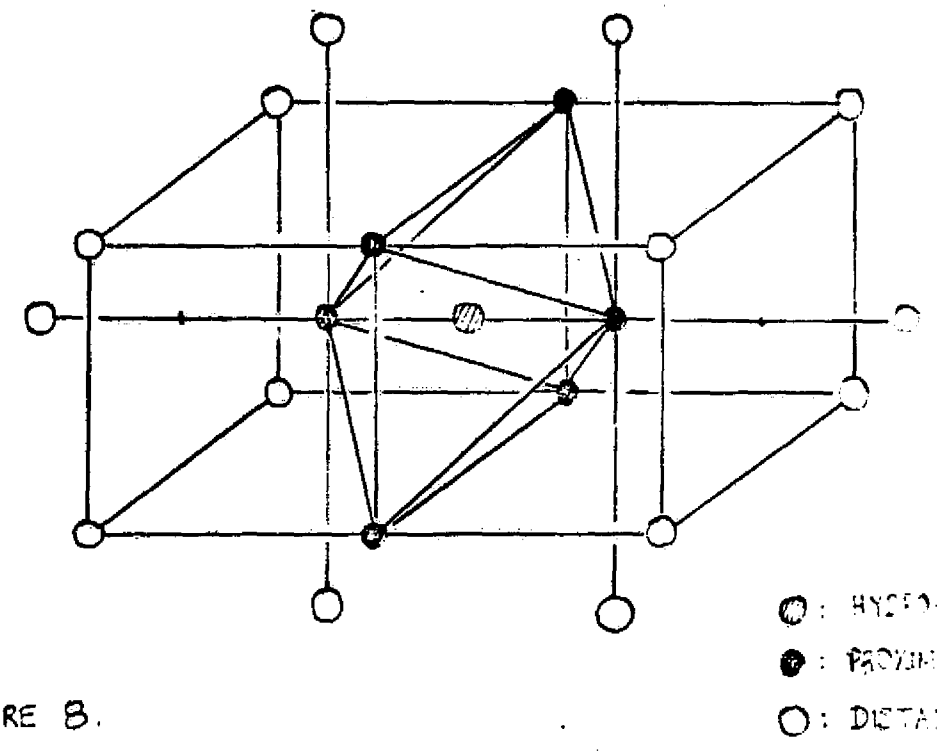


FIGURE 8.

These calculations will give direct information about the electron density redistribution in the presence of hydrogen. Moreover, from the calculated elements of the electronic energy surface, we expect to construct a rapidly convergent many-body decomposition of the form

$$E = \sum_{k} u^{(1)}(\underline{r}_k) + \sum_{k>\ell} \sum u^{(2)}(\underline{r}_k, \underline{r}_\ell) + \sum_{k>\ell\neq m} \sum \sum u^{(3)}(\underline{r}_k, \underline{r}_\ell, \underline{r}_m) + \cdots$$

which contains the important geometry dependence of the total energy surface. This is the direct ingredient to the crack simulation model.

The electronic structure calculations are being carried out in collaboration with Dr. Richard Jaffe of the NASA Ames Research Center. They employ a novel technique for folding the effects of core electrons into the form of effective potentials which makes the cluster calculations tractable by the standard methods.[7] The latter techniques are implemented using the very efficient GAUSSIAN 70 code. Finally, the magnitude of these calculations requires the special computational facilities available at NASA Ames.

We started by first checking the use of the UHF Code in dealing with the high spin cases posed by iron atom. The ground state, ^5D, can be represented in terms of real orbitals in a single determinant wavefunction

$$\mathcal{A}\left(3d^2_{xy}\alpha\beta\ 3d_{x^2-y^2}\alpha\ 3d_{xz}\alpha\ 3d_{yz}\alpha\ 3d_{3z^2-x^2-y^2}\alpha\right)$$

which contains four unpaired orbitals. The energy for this wavefunction, and various excited states, was studied as a function of the contraction in the primitive gaussian basis consisting of a 3s, 3p, and 5d functions. The results are shown in Figure 9. These results show that there is little loss in excitation energies in contracting the (335) set to [312]. This alone seems, however, to be a stricter criterion of the quality of a contraction than is necessary in calculating the ground state atom-atom interaction. We find, as shown in Figure 10, that the Fe-Fe potential energy curve is essentially identical for a [311] set as for a [312] set. Even the calculations in a minimal [111] set yield a reasonable Fe-Fe potential curve in this case.

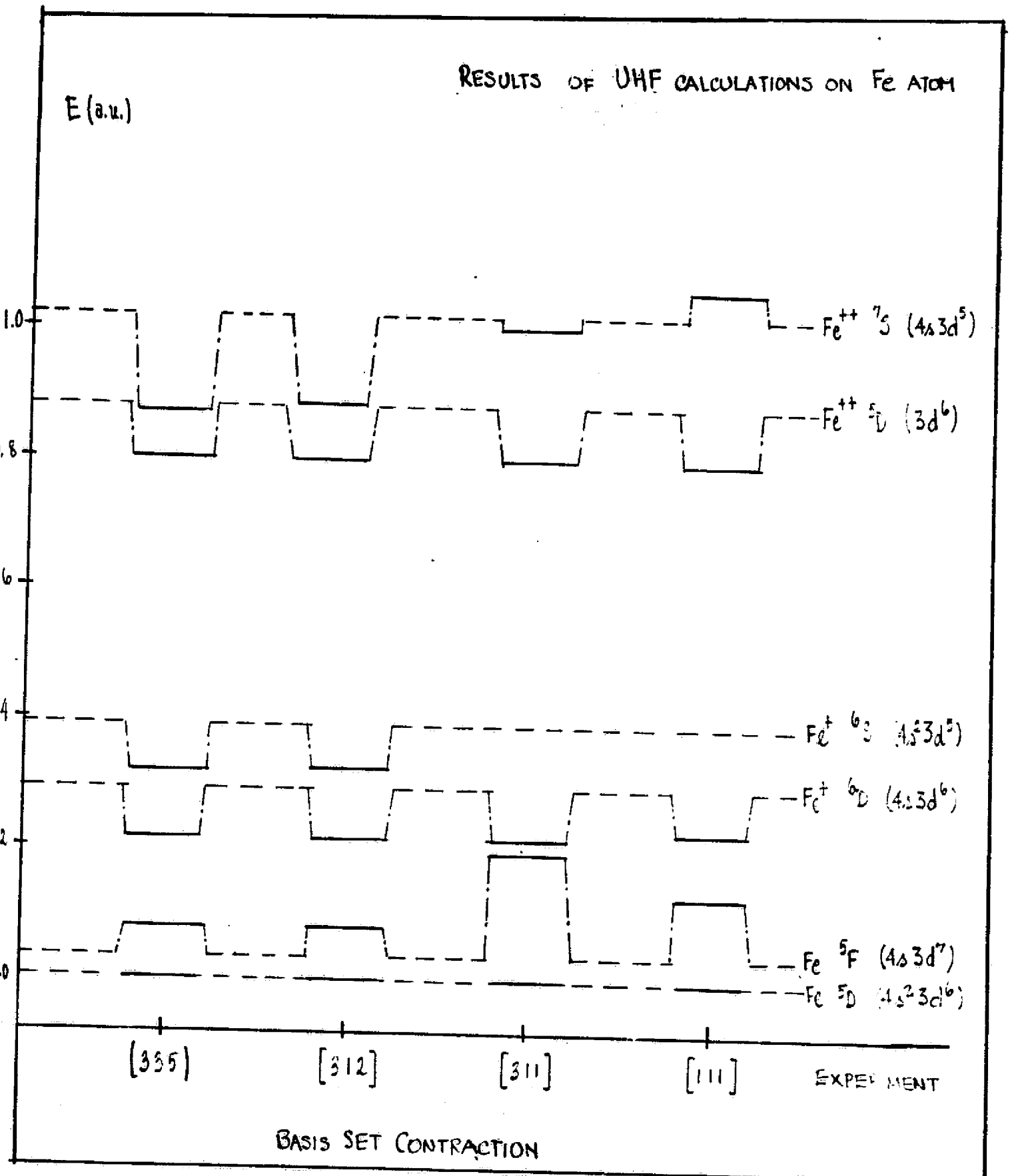

RESULTS OF UHF CALCULATIONS ON Fe ATOM
E (a.u.)
1.0
0.8
0.6
0.4
0.2
0.0
Fe^{++} ^7S ($4s3d^5$)
Fe^{++} ^5D ($3d^6$)
Fe^+ ^6S ($4s^23d^5$)
Fe^+ ^6D ($4s3d^6$)
Fe ^5F ($4s3d^7$)
Fe ^5D ($4s^23d^6$)
[333]
[312]
[311]
[111]
EXPERIMENT
BASIS SET CONTRACTION

FIGURE 9.

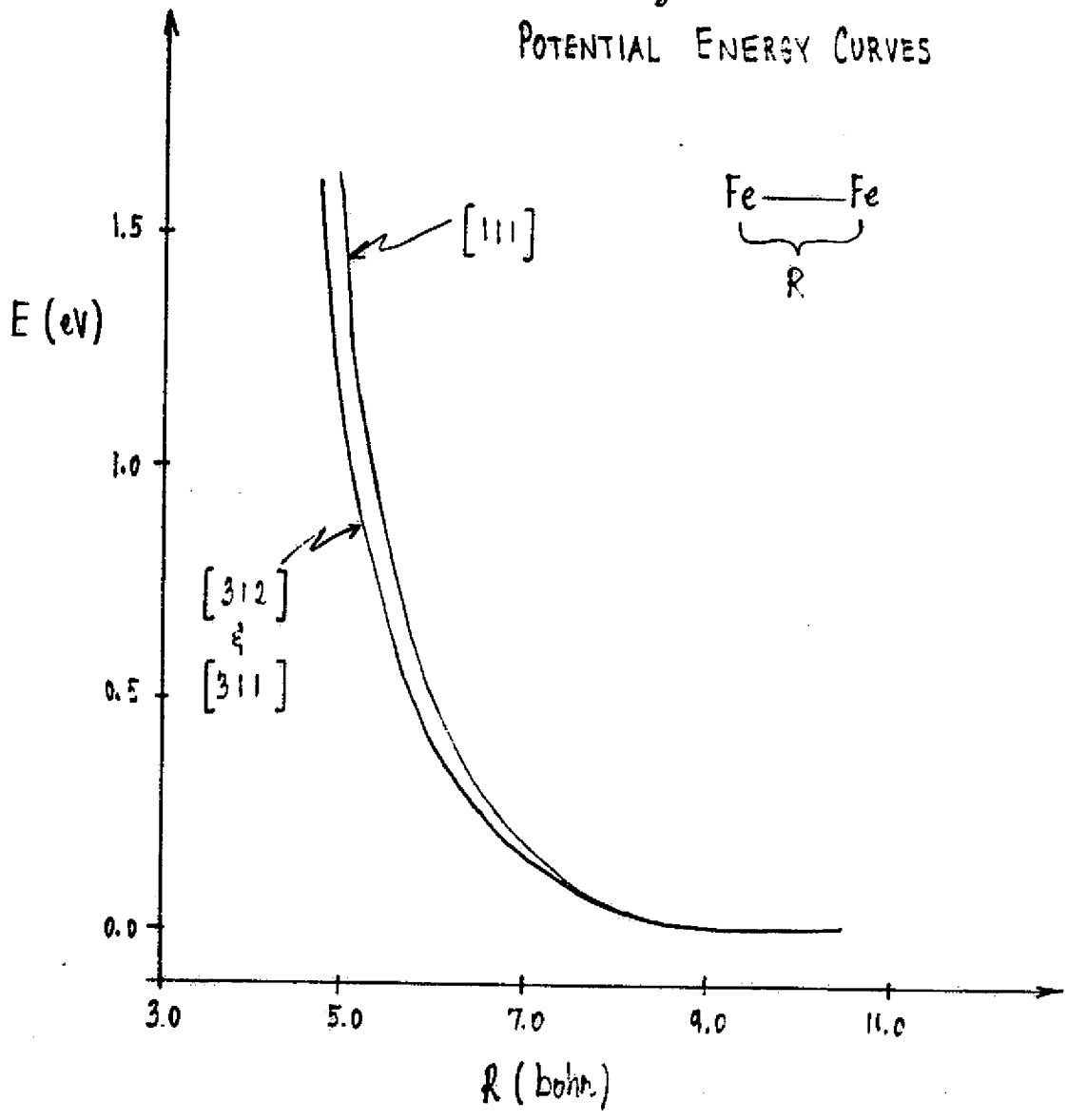

Fe_2 $^9\Sigma_g^+$
POTENTIAL ENERGY CURVES
Fe——Fe
R
[111]
[312]
[311]
E (eV)
1.5
1.0
0.5
0.0
3.0
5.0
7.0
9.0
11.0
R (bohr.)

FIGURE 10.

The lowest Fe_2 electronic state was found to be a $^9\Sigma_g^+$ state. In this state two iron d electrons remained singlet paired, and the remaining ones all align in the same direction. This high spin electron configuration is depicted schematically as

HIGH SPIN : $Fe\left[\underbrace{4s^2(1\uparrow)\,3d^6(1\uparrow 1111)}_{\uparrow}\right] + Fe\left[\underbrace{4s^2(1\uparrow)\,3d^6(1\uparrow 1111)}_{\uparrow}\right]$

The doubly occupied d orbital was found to be a d_{xz} orbital where that axis coincides with the internuclear axis. On the basis of electron repulsion arguments one would have predicted this orbital to be d_{xy}. The low spin state was compared against the high spin state at R = 5.404 bohr. The electron configuration is depicted schematically as

LOW SPIN : $Fe\left[\underbrace{4s^2(1\uparrow)\,3d^6(1\uparrow 1111)}_{\uparrow}\right] + Fe\left[\underbrace{4s^2(1\uparrow)\,3d^6(1\uparrow\uparrow\uparrow\uparrow)}_{\downarrow}\right]$

The energy of this state was found to be 0.096 Hartree/atom more repulsive than the high spin state at the same geometry.

Similar calculations were made for Fe_4 where all Fe atoms are in a plane. The [311] contraction was used since it had been found satisfactory in the Fe_2 calculations. The results are shown in Figure 11. In contrast to the Fe_2 case, we find that in Fe_4 the <u>low spin</u> state rather than the high spin state is the energetically lowest one. The intermediate spin state lies energetically between these two limits. It is interesting to note that as in the Fe_2 case, the Fe_4 energy as a function of a symmetric stretch is purely repulsive. The introduction of correlation effects will probably at least yield a Van der Waals minimum. The major effect in decreasing the repulsive energy will probably arise just from changing the geometry from planar to tetrahedral since the number of bonds between iron atoms then increases from 4 to 6.

The most interesting results were obtained upon introducing a hydrogen atom into the four iron atom cluster. The results are shown in Figure 12. The presence of the hydrogen atom stabilizes the iron cluster despite even the repulsive iron-iron interactions. It is surprising that such a large effect arises from just one additional atom. Moreover, the

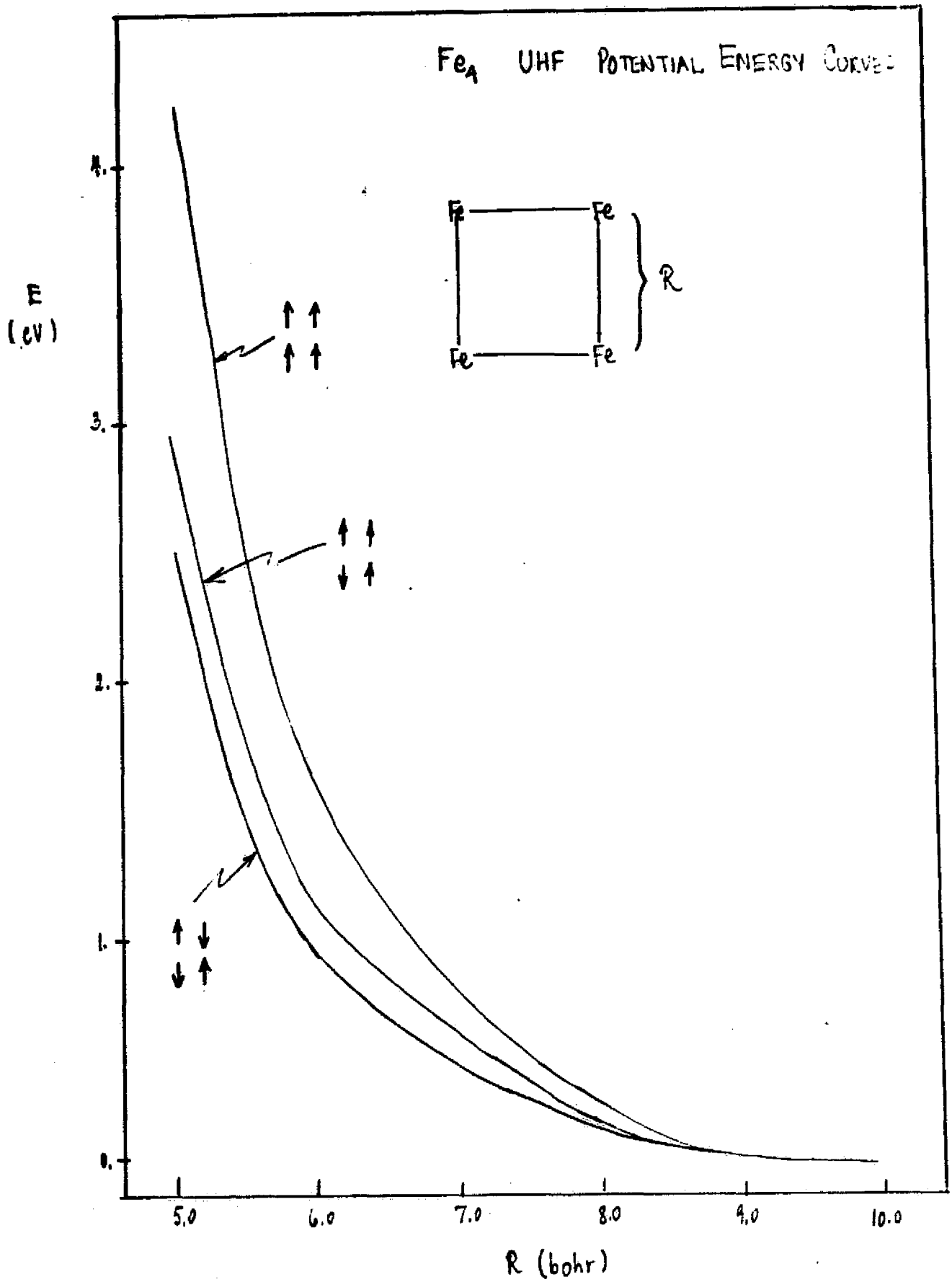

Fe_4 UHF POTENTIAL ENERGY CURVES
Fe
Fe
Fe
Fe
R
E
(eV)
4.
3.
2.
1.
0.
5.0
6.0
7.0
8.0
9.0
10.0
R (bohr)

FIGURE 11.

FIGURE 12.

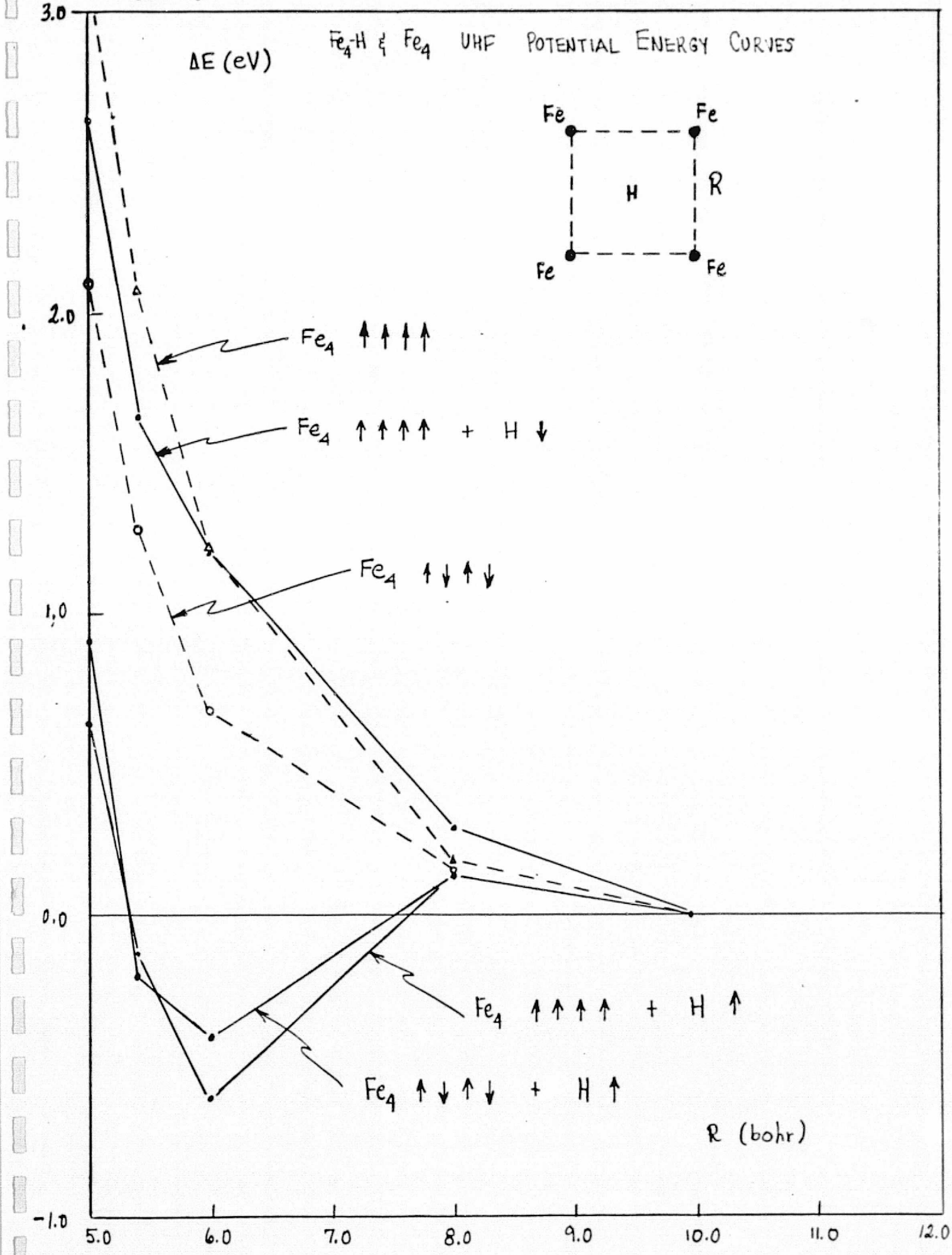
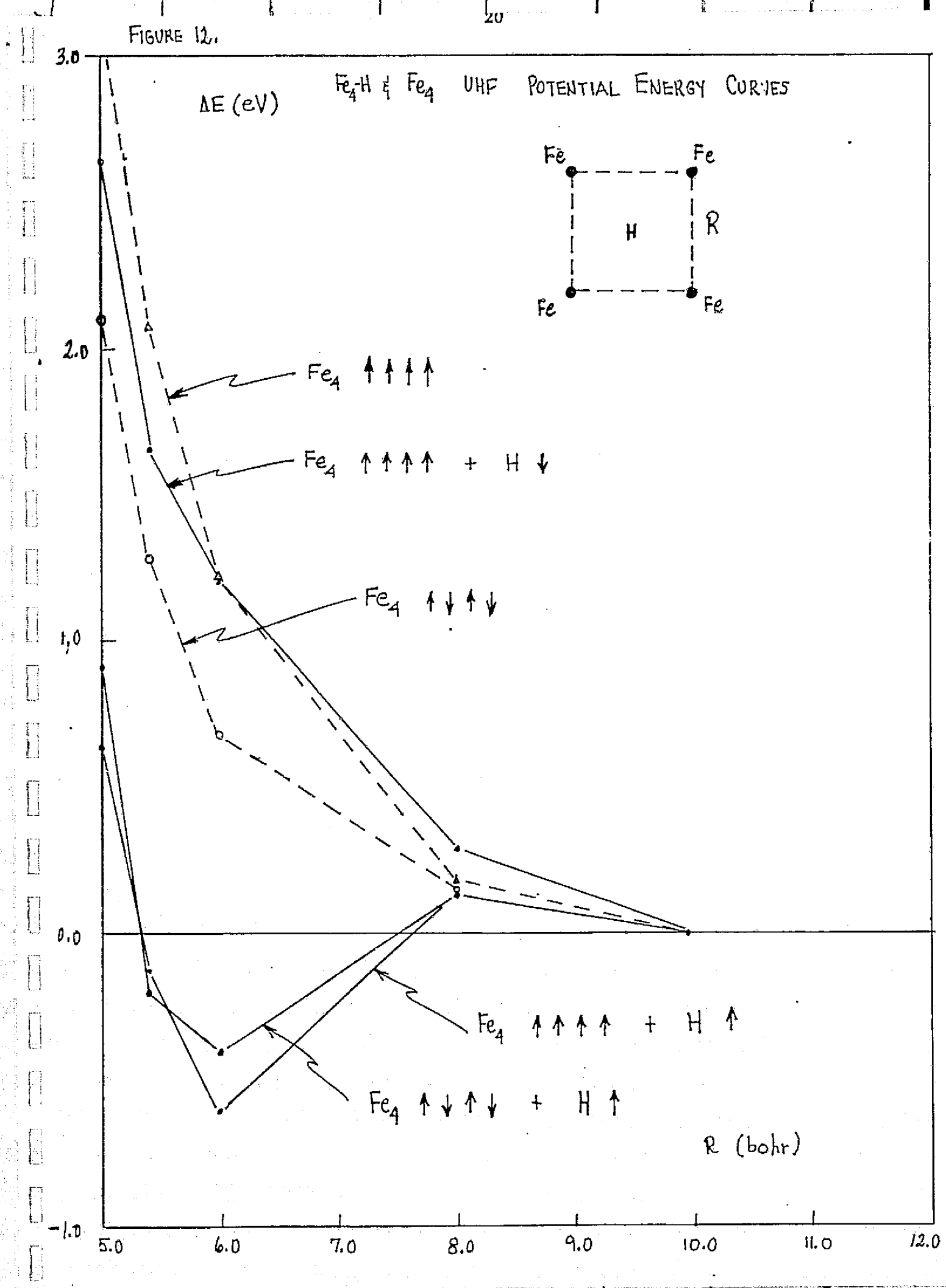

3.0
2.0
1.0
0.0
-1.0
ΔE (eV)
Fe_4-H & Fe_4 UHF POTENTIAL ENERGY CURVES
Fe
Fe
H
R
Fe
Fe
Fe_4 ↑↑↑↑
Fe_4 ↑↑↑↑ + H ↓
Fe_4 ↑↓↑↓
Fe_4 ↑↑↑↑ + H ↑
Fe_4 ↑↓↑↓ + H ↑
R (bohr)
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0

FIGURE 12.


3.0
2.0
1.0
0.0
-1.0
ΔE (eV)
Fe_4-H & Fe_4 UHF POTENTIAL ENERGY CURVES
Fe
Fe
H
R
Fe
Fe
Fe_4 ↑ ↑ ↑ ↑
Fe_4 ↑ ↑ ↑ ↑ + H ↓
Fe_4 ↑ ↓ ↑ ↓
Fe_4 ↑ ↑ ↑ ↑ + H ↑
Fe_4 ↑ ↓ ↑ ↓ + H ↑
R (bohr)
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0

effect of the hydrogen seems to be a short range effect since the cluster energy does not change until the iron atoms are about 5.6 bohr from the hydrogen atom. We also note that the high spin iron cluster becomes the lowest energy state when interacting with a hydrogen atom with spin aligned in the same direction. The opposite combination of spin alignments produces little change over the Fe_4 high spin cluster results. Insofar as the electronic structure which underlies these results is concerned, we find that there is a net charge transfer onto the hydrogen atom from the iron atoms. This is shown in Figure 13 by indicating the net number of valence electrons on each atom.

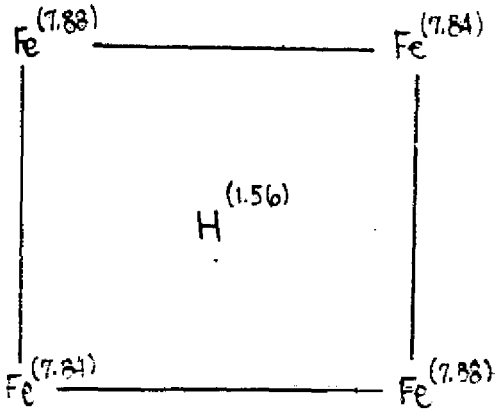


FIGURE 13.

We see that the hydrogen atom has a 0.56 increase in electron charge. The process of charge transfer is actually found to be a combination of effects. The α spin orbitals show the hydrogen atom donating 0.27 electron charges into iron 4p orbitals, while the β spin orbitals show the hydrogen atom accepting 0.83 electron changes from the iron 4s orbitals. Thus, charge transfer is an important electronic factor in the bonding of hydrogen to the iron atom cluster. Preliminary results indicate that, in contrast, a helium atom produces almost no energetic change in the iron atom cluster. This is quite reasonable given the stability of the helium atom with respect to donating or accepting extra electron charges.

Finally, we obtain also the energy surface for the motion of hydrogen atom about a fixed configuration of four iron atoms. The energy contours are shown in Figure 14. The most stable position is at the center of the cluster. The energy increases most rapidly in the direction of the iron atom. It is interesting to compare this against the results predicted by use of the pair potential superposition. We show two different empirical Fe-H pair potentials in Figure 15 together with the Fe-Fe interaction for reference. In Figures 16 and 17 we show the corresponding total energy contours resulting by use of these pair potentials. The energy surface in Figure 16 most closely resembles the present results of Figure 14. However, the predicted binding energy is three times too large. The energy surface in Figure 17 predicts that hydrogen will not be bound even at the center of the cluster. It is least in accord with the present results.

F. Definition of Terms in Formulae of Subsection C.3.

$\mathcal{D}$: set of all atoms in the discrete region

$\mathcal{C}$: set of all atoms in the continuum region

$\underset{\sim}{R}_k$: position vector of the k-th atom

∇_k : gradient operator in the $\underset{\sim}{R}_k$ coordinates

$u(D)$: interaction potential between any pair of atoms, and dpendent on just the distance between them, D.

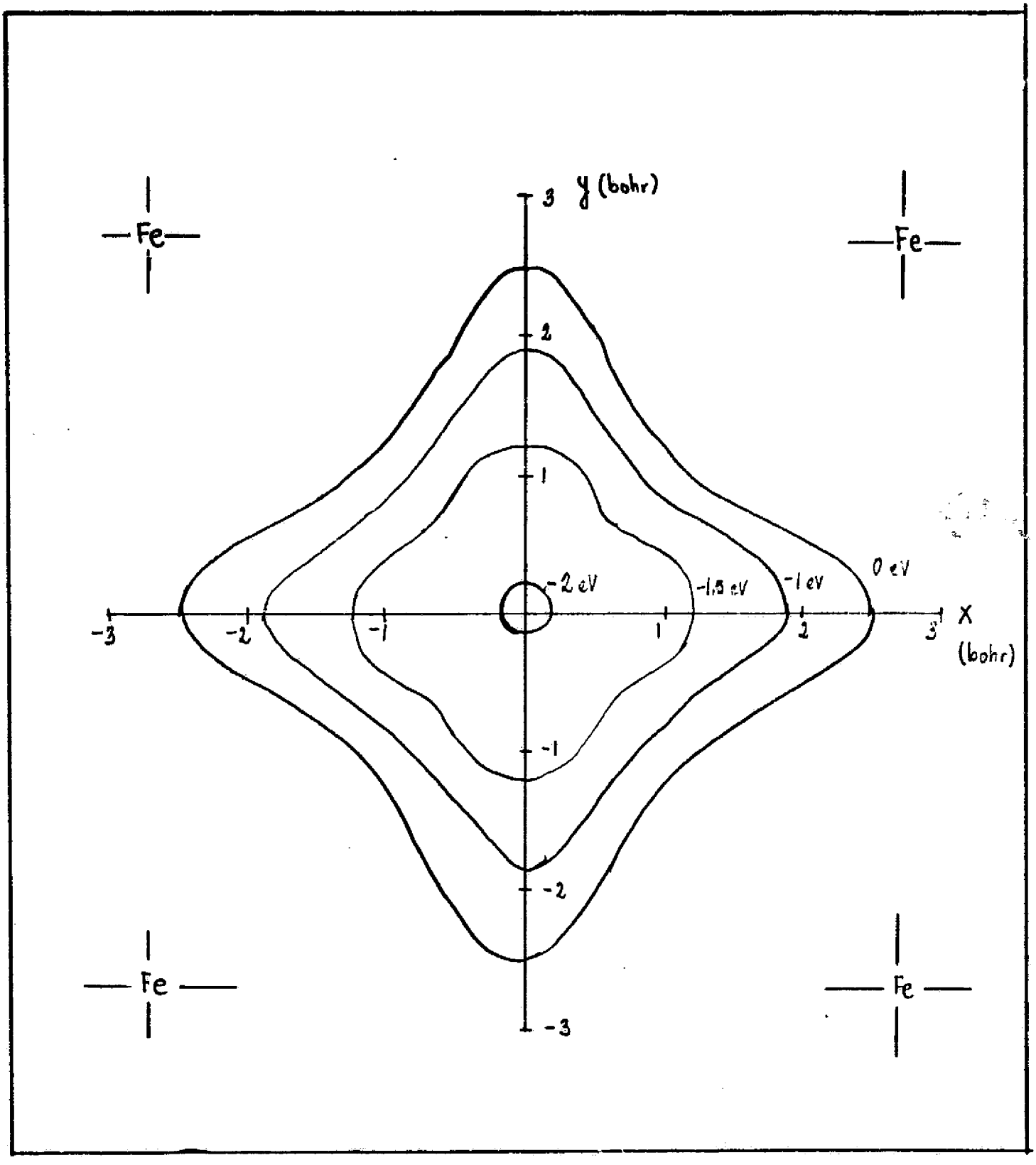


FIGURE 14. H-Fe_4 ENERGY SURFACE CONTOURS (UHF CALCULATIONS)

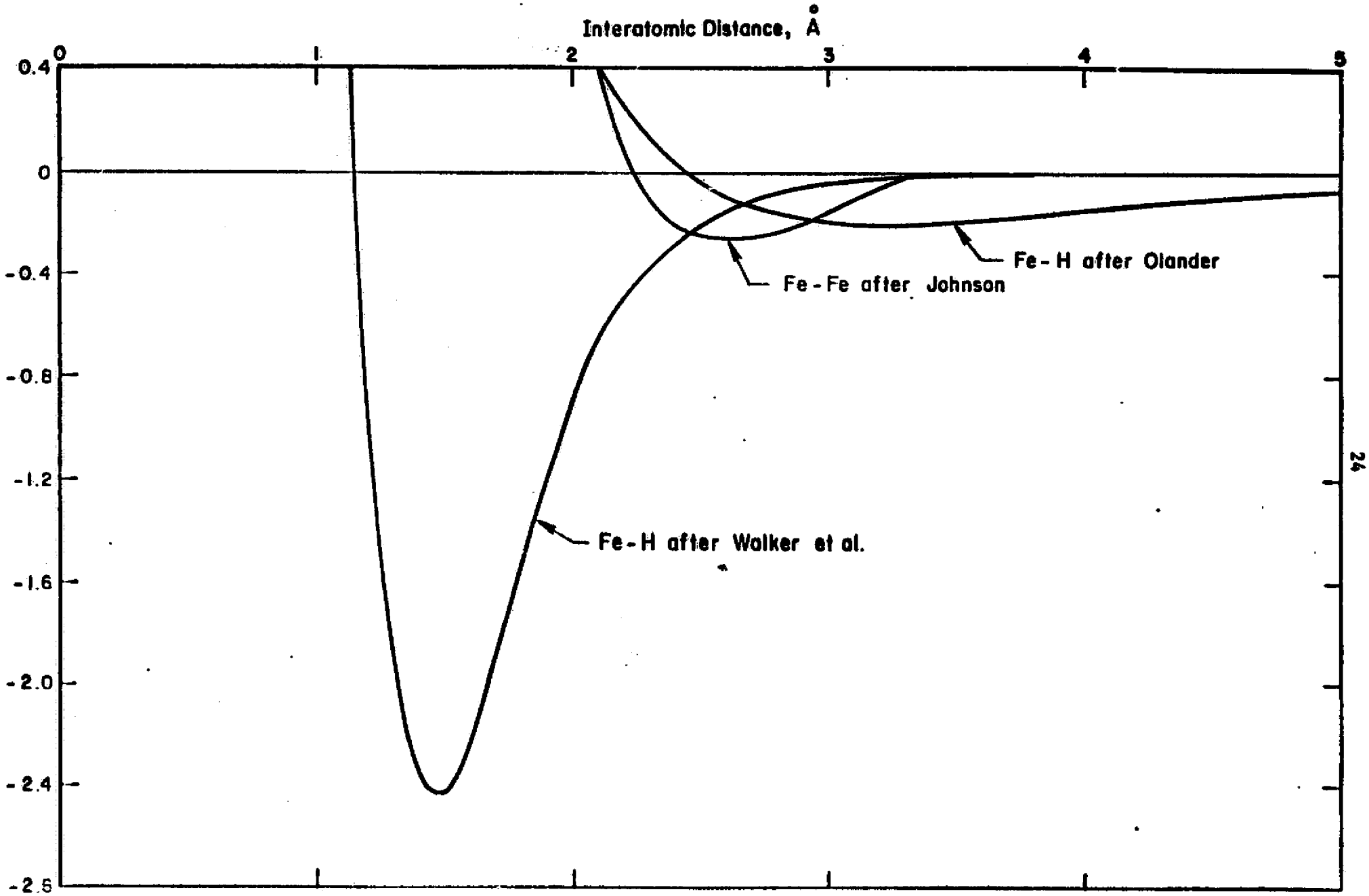

Interatomic Distance, Å
0
1
2
3
4
5
0.4
0
-0.4
-0.8
-1.2
-1.6
-2.0
-2.4
-2.8
Potential Energy, eV
Fe-H after Olander
Fe-Fe after Johnson
Fe-H after Walker et al.

FIGURE 15

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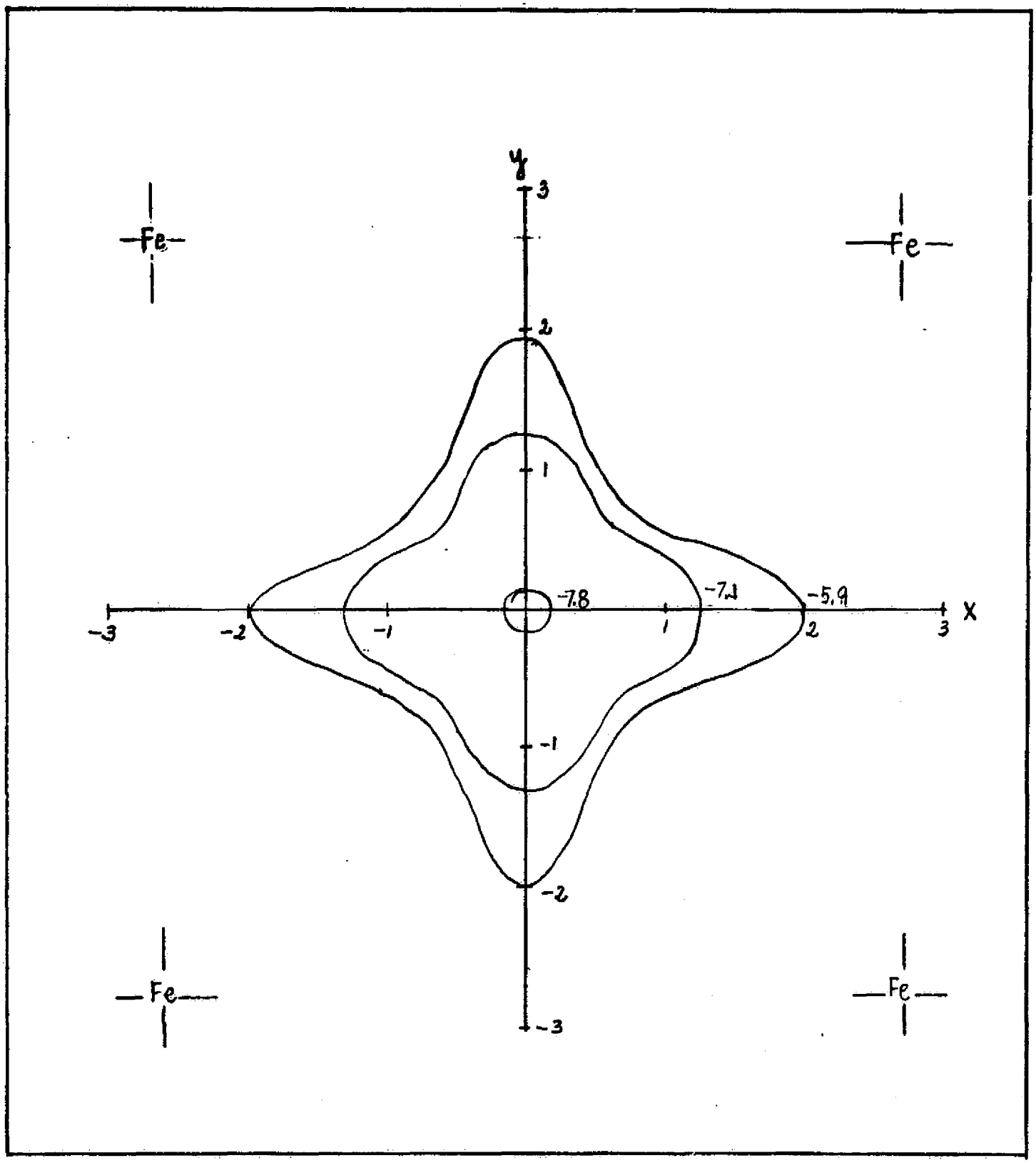

FIGURE 16. H-Fe_4 ENERGY SURFACE CONTOURS (PAIR POTENTIAL SUPERPOSITION, PAIR POTENTIAL AFTER WALKER et al.)

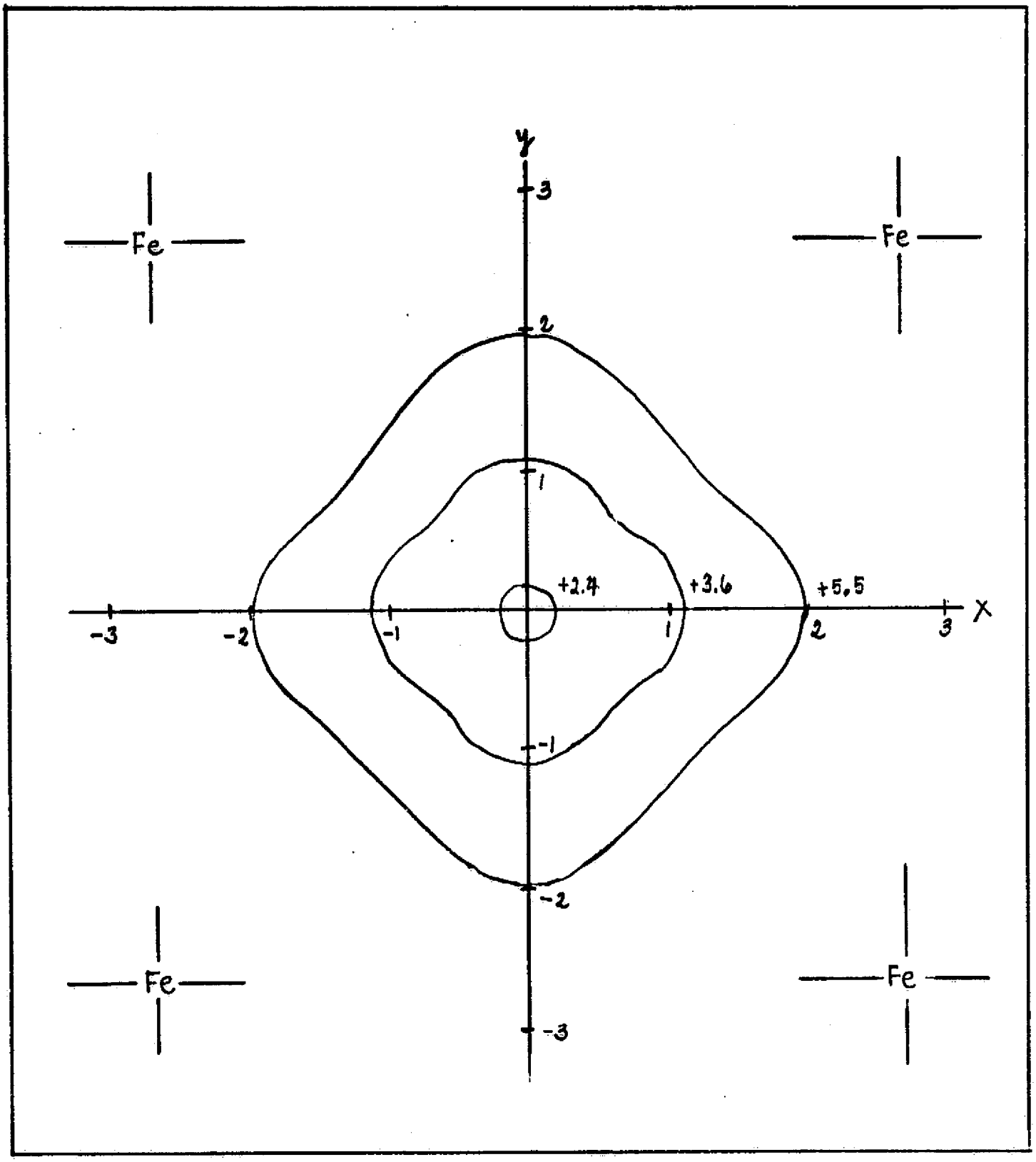

FIGURE 17. H-Fe_4 ENERGY SURFACE CONTOURS (PAIR POTENTIAL SUPERPOSITION, PAIR POTENTIAL AFTER OLANDER)

III. DIRECTIONS FOR FUTURE WORK

Dislocation motion is among the most important accepted mechanisms for the plastic deformation of metals in response to an applied stress. Gehlen found that the simulation model predicted that an edge or screw dislocation would not move even at abnormally high stresses. Our analysis of Gehlen's simulation model finds errors which are few but which fundamentally affect all results derived from its use. The improved formulation removes these errors from the model. It is thus now possible to reexamine these basic questions about dislocation motion with the improved model. With little additional effort, it is also possible to examine the manner in which an impurity atom, such as hydrogen, pins a dislocation. Beyond these questions, there are basic phenomena related to dislocation interactions, such as dislocation pile-ups and annihilations, which can readily be treated with this model.

The improved simulation model allows us also to resume on a firm basis the study of the threshold for crack propagation in iron and of the effect of hydrogen thereon. Although the errors in Gehlen's model had been identified and verified in essence, the correction factors have thus far been introduced only in an a posteriori manner. The successful solution of the dislocation and crack motion problems, will enable us to consider for the first time the crack propagation problem in the presence of a dislocation. The latter will introduce in our simulation the competing mechanism of crack energy dissipation by plastic deformation via dislocation motion.

The electronic structure calculations should explore the effect of additional shells of iron atoms, possibly with use of effective potentials to fold away the effect of all d shell electrons on outer shell iron atoms. In general, we need to develop and test rigorous systematic procedures for folding the external cluster effects, including approximations thereto, into the equations determining the electronic structure inside the clusters. We also should explore the introduction of correlation effects beyond the UHF approximation. One promising approach is the many-body perturbation method as used by Bartlett[8]. A separate but urgent problem is to develop functionals for two and three body potentials which

lead to reliable local many-body decompositions of the total energy surface. In this connection, it may be worthwhile to explore directly many-body decompositions of the electronic energy gradient as an alternative approach.

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APPENDIX

IMPROVED FORMULATION OF THE CRACK SIMULATION MODEL

Luis R. Kahn

September 30, 1977

BATTELLE
Columbus Laboratories*
Metal Science Section
505 King Avenue
Columbus, Ohio 43201

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* Research supported by NASA-Ames Research Center Under Grant NSG-2027.

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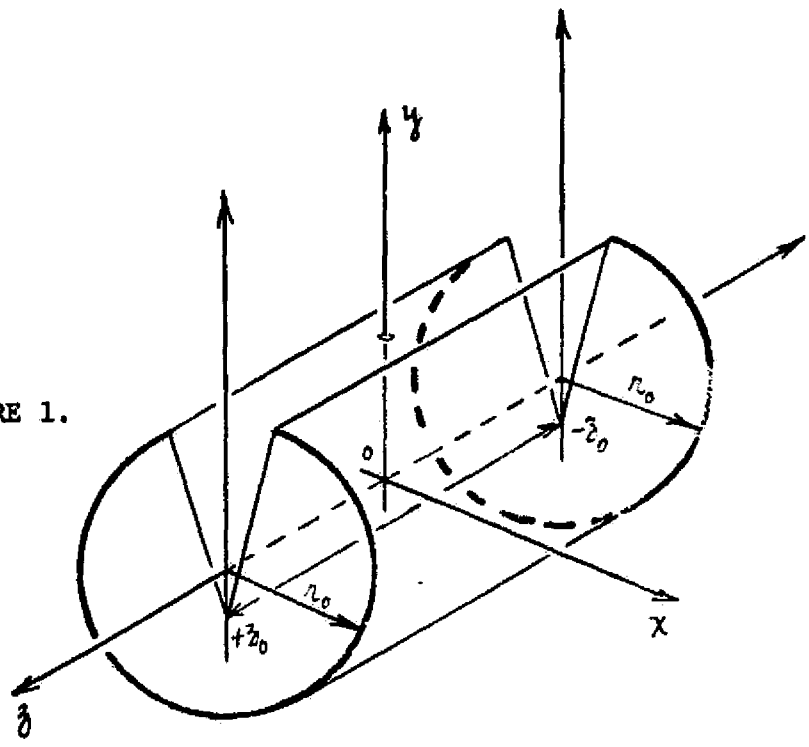
A. Definitions of regions of the model

We start by defining the different regions in the model. For this purpose we refer to Figure 1 first.

FIGURE 1.



The immediate vicinity of the defect, e.g., the crack tip, is surrounded by the cylindrical region shown above, and which is such that all points within this region have coordinates that satisfy the relationships

$$0 \leq x^2 + y^2 \leq r_0^2$$

$$-z_0 \leq z \leq +z_0$$

This region is to be called the discrete region, D. All atoms assigned to this region are to have no restriction on their optimal position except for those dictated by the interatomic forces.

Next, we have the ring-like region surrounding D as shown in **Figure 2.** All points within this region satisfy the conditions

$$r_0^2 \leq x^2 + y^2 < \infty$$

$$-z_0 \leq z \leq +z_0$$

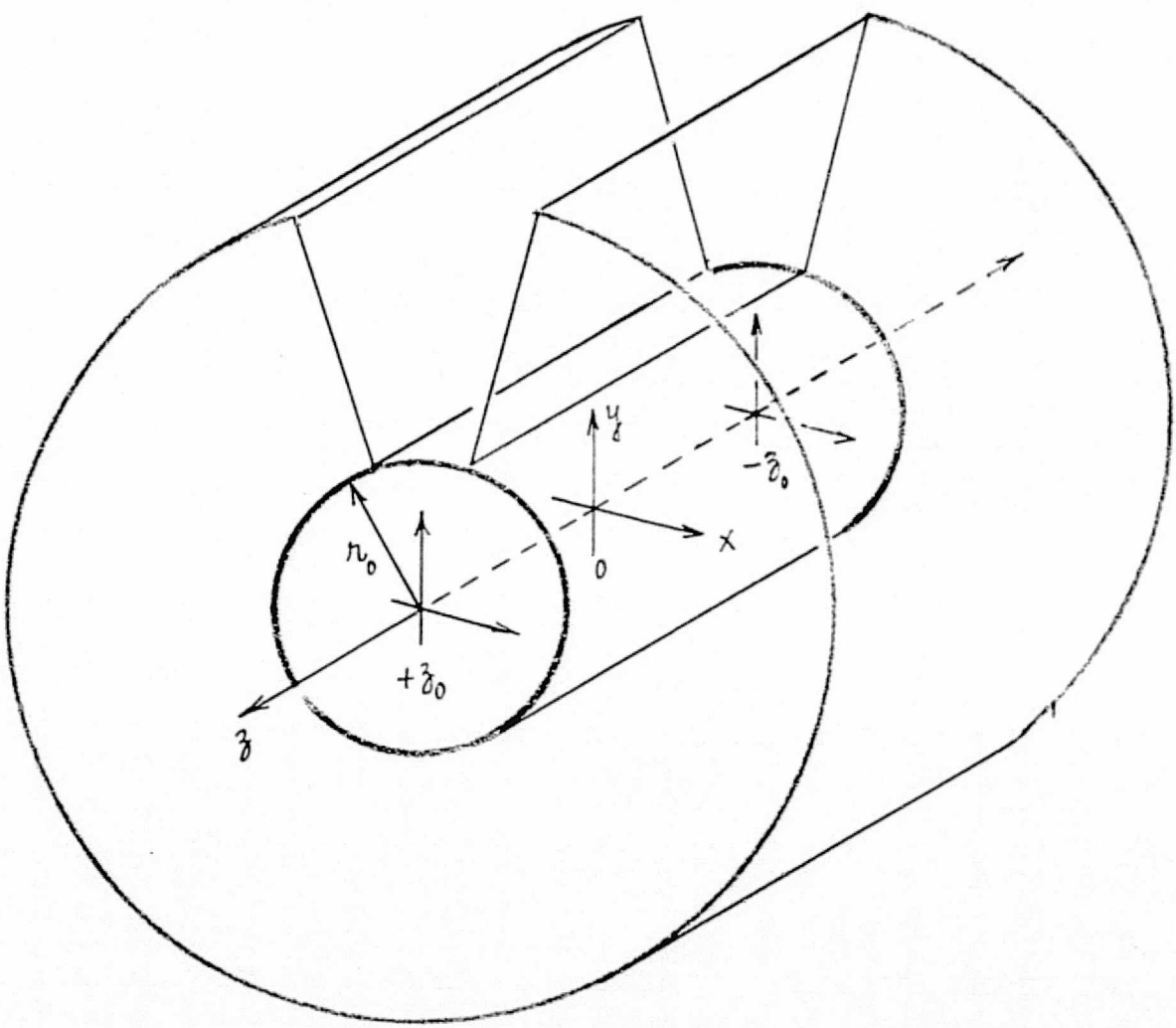


FIGURE 2.

Next, we have the ring-like region surrounding D as shown in Figure 2. All points within this region satisfy the conditions

$$r_0^2 \leq x^2 + y^2 < \alpha$$

$$-z_0 \leq z \leq +z_0$$

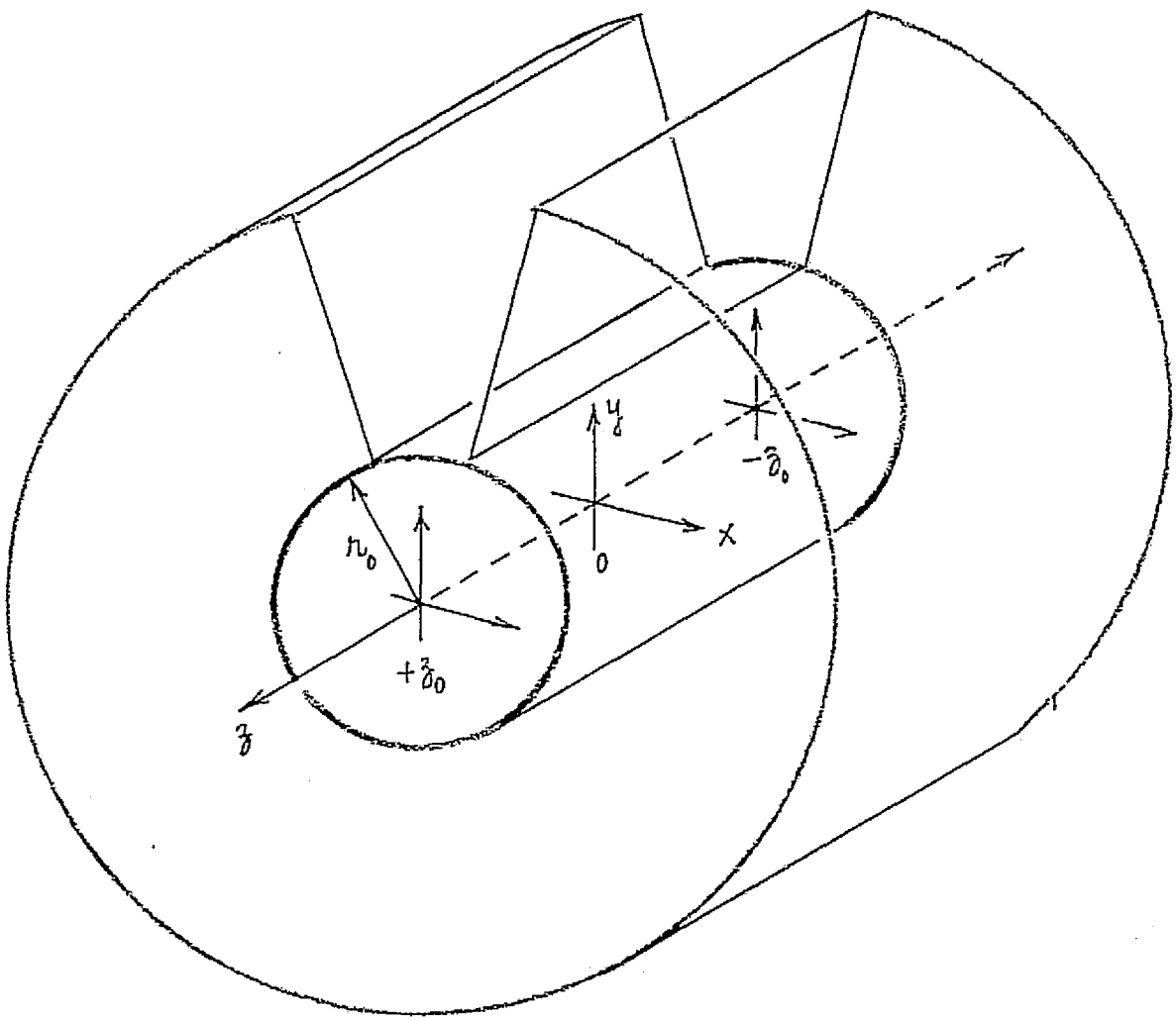


FIGURE 2.

This region is to be called the continuum region C. All atoms assigned to this region have positions dictated by elasticity theory.

Finally, there are the two regions adjacent to C and D. All points in these regions satisfy the condition

$$|z| \geq z_0$$

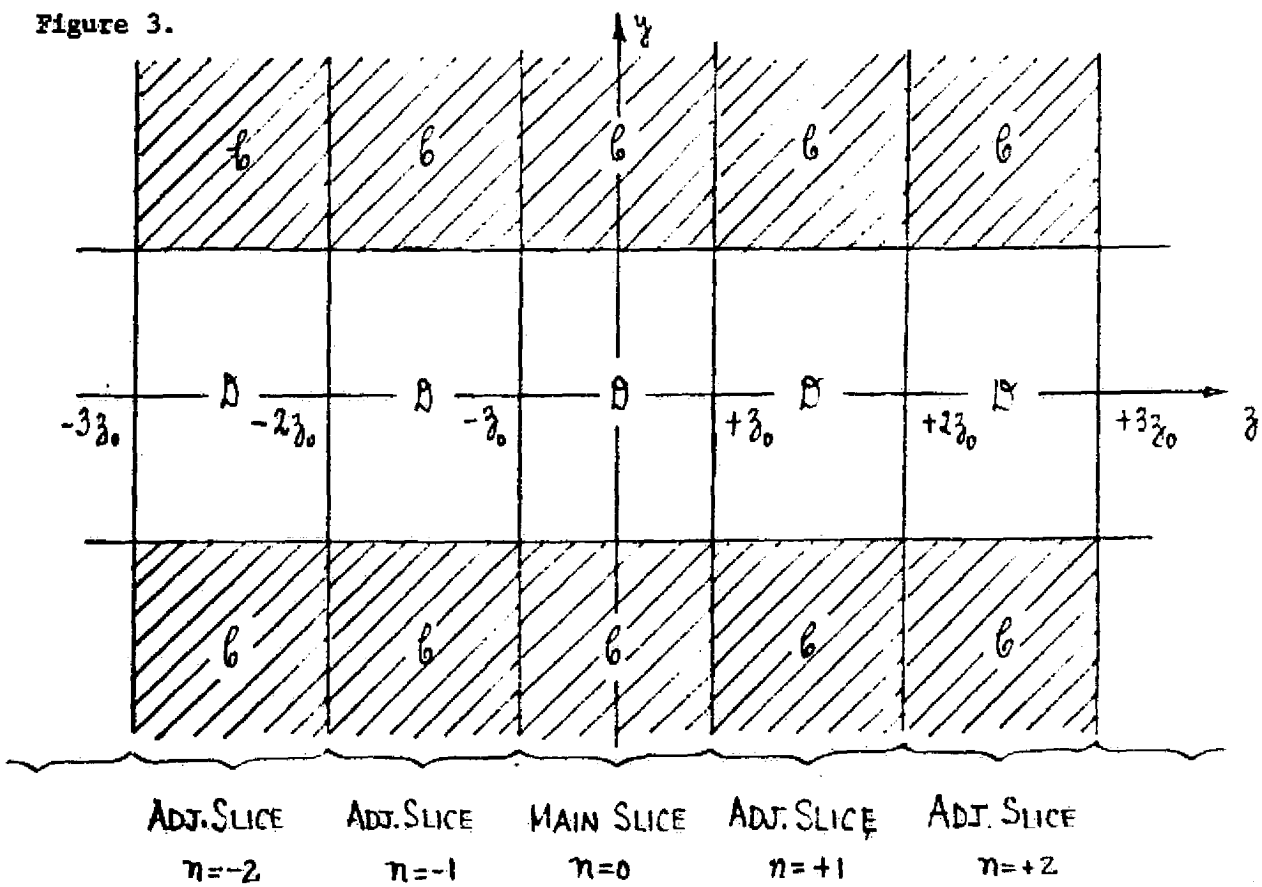
All atoms assigned to these regions have positions fixed by translational symmetry. The translation vector is written as

$$T_n = \{ 0, 0, 2nz_0 \} \qquad n = 0, \pm 1, \pm 2, \pm 3, \ldots$$

The atom positions are obtained by

$$R_k + T_n \qquad k = D \text{ or } C \qquad n = 0, \pm 1, \pm 2, \pm 3, \ldots$$

The n = 0 case gives the atoms in the main slice. The n ≠ 0 give each the atoms in the adjacent slices. This is schematically illustrated in Figure 3.



B. The configurational energy

For the present discussion we will assume that the configurational energy is given by the pair-wise interactions of all the atoms, i.e.,

$$E = \frac{1}{2} \sum_k \sum_l u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l|\right)$$

Furthermore, the configurational energy we shall be discussing is that of atoms in one slice, e.g., the main slice (MS), rather than the energy of all the atoms. In order for the configurational energy to be the same for each slice we shall include in the energy per slice half of the interaction energy with the adjacent slices (AS).

$$E = \frac{1}{2} \sum_{k \in MS} \sum_{l \in MS} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l|\right) + \frac{1}{2} \sum_{k \in MS} \sum_{l \in AS} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l|\right)$$

Upon subdividing the atoms in each slice into atoms in the D and C regions we obtain further

$$E = \frac{1}{2} \sum_{k \in D} \sum_{l \in D} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l|\right) + \frac{1}{2} \sum_{k \in C} \sum_{l \in C} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l|\right) + \sum_{k \in D} \sum_{l \in C} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l|\right)$$

$$+ \frac{1}{2} \sum_{k \in D} \sum_{l \in D} \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l - \underset{\sim}{I}_n|\right) + \frac{1}{2} \sum_{k \in C} \sum_{l \in C} \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l - \underset{\sim}{I}_n|\right)$$

$$+ \frac{1}{2} \sum_{k \in C} \sum_{l \in D} \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l - \underset{\sim}{I}_n|\right) + \frac{1}{2} \sum_{k \in C} \sum_{l \in C} \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l - \underset{\sim}{I}_n|\right)$$

This energy expression contains terms where the relevant part is embedded in a divergent series. These terms require separate analysis to follow later.

The explicitly convergent terms correspond to the energy of the discrete region and its interaction with the continuum. One can readily show that

$$\frac{1}{2} \sum_{k \in D} \sum_{l \in C} \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l - \underset{\sim}{I}_n|\right) = \frac{1}{2} \sum_{k \in C} \sum_{l \in D} \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_l - \underset{\sim}{I}_n|\right)$$

using the relation

$$\underset{\sim}{T}_{-n} = -\underset{\sim}{T}_{n}$$

Using this result one may write the explicitly convergent terms as

$$E_1 = \frac{1}{2}\sum_{k\in B}\sum_{l\in B}\left[u\left(|\underset{\sim}{R}_k-\underset{\sim}{R}_l|\right) + \sum_{\substack{n=0\\ n\neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k-\underset{\sim}{R}_l-\underset{\sim}{T}_n|\right)\right]$$

$$+\sum_{k\in B}\sum_{l\in b}\left[u\left(|\underset{\sim}{R}_k-\underset{\sim}{R}_l|\right) + \sum_{\substack{n=0\\ n\neq 0}}^{\infty} u\left(|\underset{\sim}{R}_k-\underset{\sim}{R}_l-\underset{\sim}{T}_n|\right)\right]$$

The type of interaction appearing in the first summation is represented schematically in Figure 4.

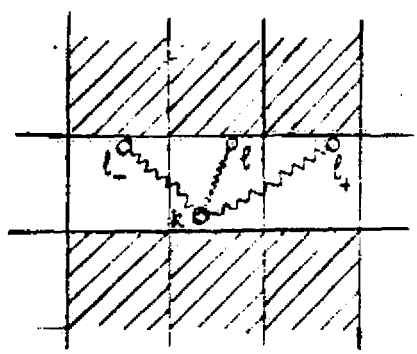


FIGURE 4.

Similarly, the second summation contains interactions shown schematically in Figure 5.

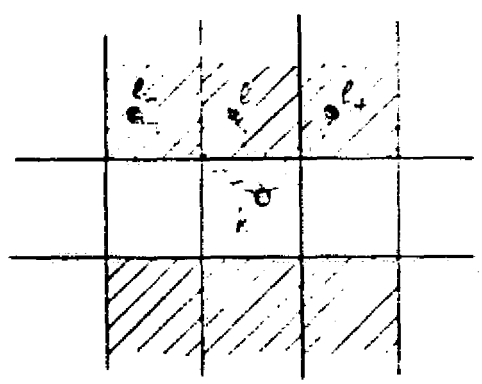


FIGURE 5.

Note that the finite range of the pair potential allows one to truncate the summation over adjacent slices to just the first pair of adjacent slices. The summation over continuum atoms can also, for the same reason, be truncated to the finite number of continuum atoms which are within the range of the pair potentials of the discrete region atoms. We shall refer to this subset of the C region atoms, as the C* region atoms.

The divergent terms in the energy correspond to the energy of the continuum region. These terms are

$$E_2 = \frac{1}{2} \sum_{k \in 6} \sum_{\ell \in 6} \left[u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) + \sum_{\substack{n=0 \\ n \neq 0}}^{-\infty} u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell - \underset{\sim}{I}_n|\right) \right]$$

The type of interaction appearing in these sums is represented schematically in Figure 6.

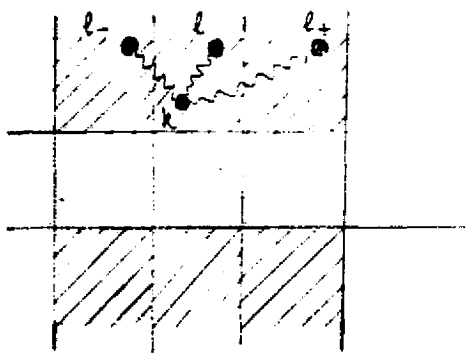


FIGURE 6.

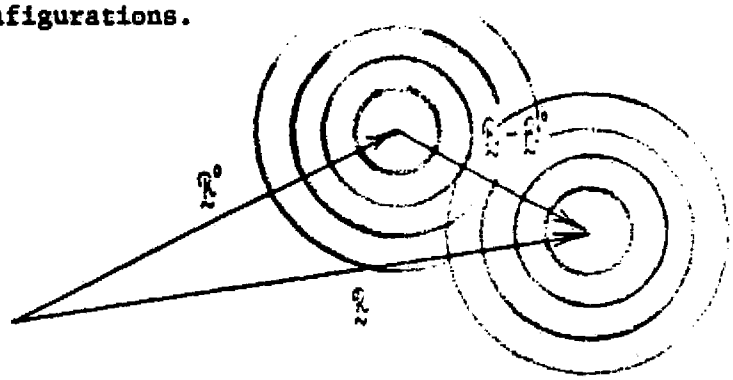
This energy is <u>infinite</u> in the stress-crack problem since it corresponds to the total strain energy of the body, and this energy diverges as the size of the body increases indefinitely. However, the <u>change</u> in the strain energy as the elastic crack field is modified is finite. Therefore, we consider the energy of the continuum configuration, $\underset{\sim}{\mathcal{R}} \in \mathcal{C}$, relative to the energy of a reference strained continuum configuration, $\underset{\sim}{\mathcal{R}}^\circ \in \mathcal{C}$, which is itself also infinite, but relative to which the energy change is finite

$$E_2\left(\underset{\sim}{\mathcal{R}} \in \mathcal{C}\right) = E_2\left(\underset{\sim}{\mathcal{R}}^\circ \in \mathcal{C}\right) + \int_{\mathcal{P}} \frac{dE_2}{d\lambda}\, d\lambda$$

The change in E_2 is a path integral of the directional derivative along a path joining the two configurations $\underset{\sim}{\mathcal{R}}$ and $\underset{\sim}{\mathcal{R}}^\circ$. This integral gives the

work energy involved in moving the system from configuration $\underset{\sim}{\xi}^0$ to configuration $\underset{\sim}{R}$.

This path integral is independent of the choice of path. We choose a conveniently simple path, namely, a straight line joining the two end-point configurations.



The locus of all points along this path is given by the vector

$$\underset{\sim}{P} = \underset{\sim}{R}^0 + \lambda\left(\underset{\sim}{R} - \underset{\sim}{\xi}^0\right) \qquad 0 \le \lambda \le 1$$

Along this path we have

(i) $s = \lambda\,|\underset{\sim}{R} - \underset{\sim}{\xi}^0|$

$$\therefore \quad \frac{ds}{d\lambda} = |\underset{\sim}{R} - \underset{\sim}{\xi}^0|$$

(ii) $$\frac{dE_2}{ds} = \frac{1}{|\underset{\sim}{R} - \underset{\sim}{\xi}^0|} \sum_{k \in \mathcal{C}} \nabla_k E_2 \cdot \left(\underset{\sim}{R}_k - \underset{\sim}{\xi}^0_k\right)$$

Using these results in the path integral we obtain

$$\int_{\mathcal{P}} \frac{dE_2}{ds}\, ds = \frac{1}{|\underset{\sim}{R} - \underset{\sim}{\xi}^0|} \int_0^1 \nabla_k E_2(\lambda) \cdot \left(\underset{\sim}{R}_k - \underset{\sim}{\xi}^0_k\right) \frac{ds}{d\lambda}\, d\lambda$$

$$= \sum_{k \in \mathcal{C}} \left(\underset{\sim}{R}_k - \underset{\sim}{\xi}^0_k\right) \cdot \int_0^1 \nabla_k E_2(\lambda)\, d\lambda$$

Thus, we have now resolved the change in the strain energy of the continuum into the contribution from each of the atoms in the continuum region. The summation over the continuum region atoms truncates to just those continuum atoms which are within the range of the pair potentials of the discrete region atoms; i.e., the atoms in the C* regions. The contribution of the continuum atoms not in C* vanishes because for these atoms

$$\nabla_k E_2 = \nabla_k E$$

and

$$\nabla_k E = 0$$

from the equilibrium condition for all points in the continuum displaced according to elasticity theory.

In summary, the configurational energy per slice is now specified precisely as

$$E = E_1 + \sum_{k \in 6^*} (\underset{\sim}{R}_k - \underset{\sim}{R}^0_k) \cdot \int_0^1 \nabla_k \Xi_2(\lambda)\, d\lambda + E_2^0$$

where

$$\nabla_k E_2(\lambda) = \sum_{\ell \in 6} \left[\nabla_k u(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \nabla_k u(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell - \underset{\sim}{I}_n|) \right] \qquad k \in 6^*$$

We shall not at present assume the equilibrium relation $\nabla_k \Xi_2 = -\nabla_k E_1$.

Approximate formulae for the work energy term may be derived by use of the trapezoidal rule and Simpson's rule for the calculation of integrals. Define

$$\underset{\sim}{F}_k = -\nabla_k E_2$$

Then applying the trapezoidal rule one finds

$$\int_0^1 \nabla_k E_2(\lambda)\, d\lambda = -\frac{1}{2}\left[\underset{\sim}{F}_k(\underset{\sim}{R}) + \underset{\sim}{F}_k(\underset{\sim}{R}^\circ) \right]$$

and applying Simpson's rule one finds

$$\int_0^1 \nabla_k E_2(\lambda)\, d\lambda = -\frac{1}{6}\left[\underset{\sim}{F}_k(\underset{\sim}{R}) + 4\,\underset{\sim}{F}_k\left(\tfrac{1}{2}\underset{\sim}{R} + \tfrac{1}{2}\underset{\sim}{R}^\circ\right) + \underset{\sim}{F}_k(\underset{\sim}{R}^\circ) \right]$$

C. Validity of the work energy formula

In truncating the work energy in E_2

$$\sum_{k\in 6} \left(\underset{\sim}{R}_k - \underset{\sim}{R}^\circ_k\right) \cdot \int_0^1 \nabla_k E_2(\lambda)\, d\lambda = \sum_{k\in 6^*} \left(\underset{\sim}{R}_k - \underset{\sim}{R}^\circ_k\right) \cdot \int_0^1 \nabla_k E_2(\lambda)\, d\lambda$$

we have assumed that

$$\nabla_k E_2 = \nabla_k E = 0$$

for all atoms in C which are not in C*. This is justified to the extent that the atom positions are given by elasticity theory, and that elasticity theory is valid in this region. We shall assume the latter since this can always be made the case by enlarging the size of region D. Insofar as the atom positions are concerned, it is basic to the model that the continuum configuration, $\underset{\sim}{R} = \underset{\sim}{\zeta}$, is given by elasticity theory. Moreover, the reference continuum configuration, $\underset{\sim}{R}^\circ = \underset{\sim}{\zeta}^\circ$, can always be chosen to satisfy elasticity theory. Thus, the integrand

$$\nabla_k E_2(\lambda) = \nabla_k E_2\left[\underset{\sim}{R}^\circ + \lambda(\underset{\sim}{R} - \underset{\sim}{R}^\circ)\right]$$

vanishes for $\lambda = 0$ and $\lambda = 1$. It is not apparent that it also vanishes for the values of λ occurring in between, $0 < \lambda < 1$. We shall show that in the case that the crack tip moves in a straight line joining the $\lambda = 0$ and $\lambda = 1$ limits, then, within the approximations of linear elasticity,

the intermediate configurations, $0 < \lambda < 1$, are in fact equilibrium configurations.

We start by specifying the end points as equilibrium configurations by writing

$$\underset{\sim}{R}^{0} = \underset{\sim}{R}^{PC} + K \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{0} \right)$$

$$\underset{\sim}{R}^{1} = \underset{\sim}{R}^{PC} + K \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{1} \right)$$

where $\underset{\sim}{R}^{PC}$ are the perfect crystal positions of the atoms, $\underset{\sim}{t}$ is the position of the crack tip, and $\underset{\sim}{w}$ stands for the displacement field given by linear elasticity. All intermediate equilibrium configurations are obtained from

$$\underset{\sim}{R} = \underset{\sim}{R}^{PC} + K \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t} \right)$$

note that

$$\underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t} \right) = \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{0} + \Delta \underset{\sim}{t}^{0} \right)$$

$$= \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{0} \right) + \nabla \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{0} \right) \cdot \Delta \underset{\sim}{t}^{0} + \cdots$$

where

$$\Delta \underset{\sim}{t}^{0} = \underset{\sim}{t} - \underset{\sim}{t}^{0}$$

Similarly, we also have

$$\underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t} \right) = \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{1} \right) + \nabla \underset{\sim}{w}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^{1} \right) \cdot \Delta \underset{\sim}{t}^{1} + \cdots$$

where

$$\Delta \underset{\sim}{t}^1 = \underset{\sim}{t} - \underset{\sim}{t}^1$$

Therefore we can write both

$$\underset{\sim}{R} = \underset{\sim}{R}^0 + K \nabla \underset{\sim}{W}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^0 \right) . \Delta \underset{\sim}{t}^0 + \cdots$$

and

$$\underset{\sim}{R} = \underset{\sim}{R}^1 + K \nabla \underset{\sim}{W}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^1 \right) . \Delta \underset{\sim}{t}^1 + \cdots$$

Next, we choose the crack tip to arrive along a line joining the endpoint crack-tip positions

$$\underset{\sim}{t} = \underset{\sim}{t}^0 + \lambda \left(\underset{\sim}{t}^1 - \underset{\sim}{t}^0 \right) \qquad 0 \leq \lambda \leq 1$$

Using this in the equations for $\underset{\sim}{R}$, and expanding $\nabla \underset{\sim}{W}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^1 \right)$ about $\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^0 \right)$ one finds

$$\underset{\sim}{R} = \underset{\sim}{R}^0 + \lambda K \nabla \underset{\sim}{W}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^0 \right) . \left(\underset{\sim}{t}^1 - \underset{\sim}{t}^0 \right) + \cdots$$

and

$$\underset{\sim}{R} = \underset{\sim}{R}^1 + (\lambda - 1) K \nabla \underset{\sim}{W}\left(\underset{\sim}{R}^{PC} - \underset{\sim}{t}^0 \right) . \left(\underset{\sim}{t}^1 - \underset{\sim}{t}^0 \right) + \cdots$$

Neglecting all terms which are second and higher order changes in $\underset{\sim}{W}$, as is consistent with linear elasticity, and subtracting both equations, after first dividing each by λ and $(\lambda - 1)$ respectively, we obtain

$$\frac{1}{\lambda}\left(\underset{\sim}{R}-\underset{\sim}{R}^{0}\right)=\frac{1}{\lambda-1}\left(\underset{\sim}{R}-\underset{\sim}{R}^{1}\right)$$

or

$$\underset{\sim}{R}=\underset{\sim}{R}^{0}+\lambda\left(\underset{\sim}{R}^{1}-\underset{\sim}{R}^{0}\right)$$

This shows that, within the assumptions of linear elasticity, the configurations generated by passing a straight line between two equilibrium configurations are themselves equilibrium configruations associated with a crack tip which is also moving on a straight line.

D. A new approach to the search for the equilibrium configuration

One of the important lessons from our past work is that the continuum elastic field, in which the discrete region is embedded, cannot be left positioned arbitrarily. The effect of variously positioning the elastic field, followed in each case by a full relaxation of the discrete region, leads to energy changes of the very same magnitude as the energy differences we are interested in. It is clear that the position of the continuum field has to be carefully adjusted in direct concert with the relaxations occurring in the discrete region. The aim is to minimize the disregistry between the fields in the two regions.

The configurational energy (potential energy) of the model, which was discussed in section B, depends directly on the position of the continuum field through the positions of the atoms in this region. It is therefore possible to attain minimal disregistry simply as part of the process of seeking for the lowest total potential energy in all variables, i.e., including the position of the continuum field with the other degrees of freedom relative to which the system is being relaxed. This approach affords a unified treatment of the approach to equilibrium of the discrete and continuum regions. This unity of approach extends to the introduction of non-linear effects in the elastic field. In this more general case, the parameters adjusting the char-

acter and admixture of non-linear elastic field terms are simply to be added (in the list of variables to be relaxed) to the position of the overall field and the positions of the atoms in the discrete region.

In the pioneering simulation work of P. C. Gehlen[1], the discrete and continuum regions were cast in a mold which naturally pointed to separate and distinct procedures for relaxing each region. Thus, the discrete region was relaxed using the technique of "kinetic energy quenching" by Larsen[2], while the continuum was relaxed (in the flexible boundary version) by generating, via Green's functions, the displacement fields which drove all the current non-zero forces to zero. These two processes were used sequentially until the system was found in equilibrium.

In the present approach, as also in the simulation work of Sinclair[3], all distinct properties of each region are built in at the outset in the configurational energy functional. Thereafter, the search for equilibrium becomes a problem of minimization of this functional with little remaining distinction between the discrete and continuum regions. One approach which seems practical for a function minimization involving as many independent variables as found in the crack simulation (300 - 1000) is the method of "conjugate gradients" of Fletcher and Reeves[4]. This method requires in essence only the calculation of the gradients of the potential energy in order to lead to a minimum. It involves a sequence of search direction vectors (constructed from the gradient information) and one-dimensional function minimizations in these directions. Define the gradient vector as

$$\underset{\sim}{G} = \nabla E = \left(\nabla_1 E, \nabla_2 E, \ldots, \nabla_n E \right)$$

where E is the configurational energy functional defined in section B, and the gradient vector has a component for each linearly independent variable in E. The Fletcher and Reeves algorithm is

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$i = 0, 1, 2, \ldots$

$$\underset{\sim}{R}_{i+1} = \left(\text{POSITION OF THE MINIMUM OF } [\text{illegible}] \text{ THROUGH } \underset{\sim}{R}_i \text{ IN THE DIRECTION } \underset{\sim}{S}_i \right)$$

$$\underset{\sim}{G}_{i+1} = \underset{\sim}{G}\left(\underset{\sim}{R}_{i+1}\right)$$

$$\underset{\sim}{S}_{i+1} = -\underset{\sim}{G}_{i+1} + \left(\frac{\underset{\sim}{G}_{i+1} \cdot \underset{\sim}{G}_{i+1}}{\underset{\sim}{G}_{i} \cdot \underset{\sim}{G}_{i}}\right) \underset{\sim}{S}_{i}$$

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where $\underset{\sim}{R}_0 =$ { INITIAL GUESS OF THE EQUILIBRIUM CONFIGURATION }

$$\underset{\sim}{G}_0 = \underset{\sim}{G}\left(\underset{\sim}{R}_0\right)$$

$$\underset{\sim}{S}_0 = -\underset{\sim}{G}_0$$

This function minimization method also has the advantage of requiring but relatively minor modification to serve in finding saddle points. It then becomes the method of Sinclair and Fletcher[5]. A closely related function minimization algorithm is that of Fletcher and Powell[6]. Although this latter algorithm may be generally more stable and rapidly convergent there is a price. It requires at each step the additional construction and manipulation of a full (symmetric positive definite) matrix which at convergence becomes the inverse of the Hessian matrix. Moreover, one requires $N(N+1)/2$ additional storage spaces, where N is the number of independent variables. This limits the application of the Fletcher and Powell method to cases for which $N \lesssim 400$.

A method which has been successfully used in the past to find equilibrium configurations is the "kinetic energy quenching" method of Larsen[2]. This method is based on the integration of the classical equations of motion as a convenient device to enable the atoms to probe the configurational energy surface. This is coupled with periodic removals of the accumulated kinetic energy until the system is at a potential energy minimum. While the classical-equations-of-motions method is straight forward when applied to the motion of the atoms in the discrete region, such is not the case when, as in the present approach, we also wish to relax by the same procedure the parameters of the continuum elastic field. We show next that indeed it is possible to extend this method to deal directly with the elastic field.

The kinetic energy of the system is the kinetic energy of the atoms in the discrete and continuum regions respectively

$$K = \sum_{k \in B} \frac{1}{2} m_k \dot{\underset{\sim}{R}}_k \cdot \dot{\underset{\sim}{R}}_k + \sum_{k \in C} \frac{1}{2} m_k \dot{\underset{\sim}{R}}_k \cdot \dot{\underset{\sim}{R}}_k$$

We constrain all points of the continuum region to be displaced according to an elastic field specified by a set of m parameters, $\underset{\sim}{s} = (s_1, s_2, \ldots, s_m)$ i.e.,

$$\underset{\sim}{R}_k = \underset{\sim}{R}_k(\underset{\sim}{s}) \qquad k \in C$$

We define the mass tensor

$$I_{\alpha\beta} = \sum_{k \in C} m_k \frac{\partial \underset{\sim}{R}_k}{\partial s_\alpha} \cdot \frac{\partial \underset{\sim}{R}_k}{\partial s_\beta} = I_{\beta\alpha} \qquad \alpha, \beta = 1, 2, \ldots, m$$

The kinetic energy may now be written as

$$K = \sum_{k \in B} \frac{1}{2} m_k \dot{\underset{\sim}{R}}_k \cdot \dot{\underset{\sim}{R}}_k + \frac{1}{2} \dot{\underset{\sim}{s}} \underset{\sim}{\underset{\sim}{I}} \dot{\underset{\sim}{s}}$$

where the kinetic energy contribution from the continuum atoms is now expressed in terms of the mass tensor and the time rate of change of the parameters of the elastic field. Next we define the momentum associated with each of the degrees of freedom.

$$\underset{\sim}{P}_k = \frac{\partial K}{\partial \dot{\underset{\sim}{R}}_k} = m_k \dot{\underset{\sim}{R}}_k$$

$$\underset{\sim}{\underset{\sim}{P}}_s = \frac{\partial K}{\partial \dot{\underset{\sim}{s}}} = \underset{\sim}{\underset{\sim}{I}}\, \dot{\underset{\sim}{s}}$$

Reexpressing the kinetic energy in terms of the momenta we find

$$K = \sum_{k \in B} \frac{1}{2m_k} \underset{\sim}{P}_k \cdot \underset{\sim}{P}_k + \frac{1}{2} \underset{\sim}{\underset{\sim}{P}}_s \underset{\sim}{\underset{\sim}{I}}^{-1} \underset{\sim}{\underset{\sim}{P}}_s$$

The hamiltonian is

$$H = K + E$$

where E is the configurational or potential energy discussed in section B. The equations of motion for the atoms in the discrete region are

$$\dot{\underset{\sim}{R}}_k = \frac{\partial H}{\partial \underset{\sim}{P}_k} = \frac{1}{m_k} \underset{\sim}{P}_k \qquad k \in B$$

$$\dot{\underset{\sim}{P}}_k = -\frac{\partial H}{\partial \underset{\sim}{R}_k} = -\nabla_k E$$

These are just the standard classical equations of motion. In addition, we also find the new result we are seeking, namely the equations of motion for the elastic field parameters. These are:

$$\dot{\underset{\sim}{s}} = \frac{\partial H}{\partial \underset{\sim}{p}_s} = \underset{\sim}{I}^{-1} \underset{\sim}{p}_s$$

$$\dot{\underset{\sim}{p}}_s = -\frac{\partial H}{\partial \underset{\sim}{s}} = -\frac{\partial K}{\partial \underset{\sim}{s}} - \frac{\partial E}{\partial \underset{\sim}{s}}$$

where

$$\frac{\partial K}{\partial s_\alpha} = \frac{1}{2} \underset{\sim}{p}_s \cdot \frac{\partial \underset{\sim}{I}^{-1}}{\partial s_\alpha} \underset{\sim}{p}_s$$

$\alpha = 1, 2, \ldots, n$

and

$$\frac{\partial E}{\partial s_\alpha} = \sum_{k \in i^*} \nabla_k E \cdot \frac{\partial \underset{\sim}{R}_k}{\partial s_\alpha}$$

This specifies all the ingredients necessary to extend the kinetic energy quench method to the direct relaxation of the elastic field. It shows that each parameter of the elastic field obeys equations of motion similar to those for the atoms in the discrete region. In this sense these parameters behave as pseudo-atoms with inertia given by the mass tensor $\underset{\sim}{I}$, and subject to driving forces that arise partly from the potential energy, E, and partly from the elastic field dependence of the mass tensor.

The present result shows that the "kinetic energy quench" procedure may be applied to relax <u>all</u> regions of the model. It is a viable alternative to the use of the "conjugate gradients" approach of Fletcher and Reeves. In

fact there are scattered results based on the previous simulation approach indicating that the rate of convergence of the "kinetic energy quench" procedure may be considerably faster than obtained from the Fletcher and Reeves approach. This probably is the case at least in the early stages of the relaxation, and suggests the sequential use of these two techniques for optimal convergence to equilibrium.

Although the present extension of the equations of motions method is primarily designed as an aid to find the equilibrium positions, it may also contain the seeds for a bona fide modelling of time dependent crack processes.

E. The gradient of the configurational energy.

The gradient of the energy turns out to be a sufficient and central ingredient in the two principal methods for relaxing the system to its equilibrium configurations (both to relative minimums and to saddle points). We show here the relationship of the gradient of the energy to the gradients of the individual pair potentials.

The components of the gradient of the energy vector are the partial derivatives of the energy with respect to all the linearly independent parameters in the energy. These are the positions of the atoms in the discrete region

$$\underset{\sim}{R}_k \qquad k \in \mathcal{N}$$

and the parameters specifying the elastic field which we shall denote by

$$\underset{\sim}{t} = (t_1, t_2, \ldots, t_m)$$

Three of these parameters we shall always take as the coordinates of the origin of the elastic field. Parameters beyond these correspond to non-linear elatic field terms.

The gradient component in a discrete region atom coordinate is

$$\nabla_k E = \sum_{l \in B} \left[\nabla_k u(|R_k - R_l|) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \nabla_k u(|R_k - R_l - T_n|) \right]$$

$$+ \sum_{l \in C} \left[\nabla_k u(|R_k - R_l|) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \nabla_k u(|R_k - R_l - T_n|) \right] \qquad k \in B$$

The gradient component in an elastic field parameter is related by the chain rule to gradients of the energy in the atom coordinates

$$\frac{\partial E}{\partial t_\alpha} = \sum_{k \in B} \nabla_k E \cdot \frac{\partial R_k}{\partial t_\alpha} + \sum_{k \in C} \nabla_k E \cdot \frac{\partial R_k}{\partial t_\alpha} \qquad \alpha = 1, 2, \ldots, m$$

The sum over discrete region atoms vanishes because of linear independence, i.e.,

$$\frac{\partial R_k}{\partial t_\alpha} = 0 \qquad k \in B \quad , \quad \alpha = 1, 2, \ldots, m$$

The second sum ranges just over the atoms in C which interact with region D atoms, C*, because for all others in C we have

$$\nabla_k E = 0$$

from the equilibrium condition assumed for the continuum. Therefore, we find

$$\frac{\partial E}{\partial t_\alpha} = \sum_{k \in C^*} \nabla_k E \cdot \frac{\partial R_k}{\partial t_\alpha} \qquad \alpha = 1, 2, \ldots, m$$

where the gradients of the energy in a continuum region atom coordinates is

$$\nabla_k E = \sum_{\ell \in B} \left[\nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell - \underset{\sim}{I}_n|\right) \right]$$

$$+ \sum_{\ell \neq k} \left[\nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell|\right) + \sum_{\substack{n=-\infty \\ n \neq 0}}^{\infty} \nabla_k u\left(|\underset{\sim}{R}_k - \underset{\sim}{R}_\ell - \underset{\sim}{I}_n|\right) \right]$$

A particular combination of the gradients which is required in the one-dimensional searches of the "conjugate gradient" method is the directional derivative. This is

$$\Delta \frac{dE}{d\delta} = \sum_{k \in B} \nabla_k E \cdot \underset{\sim}{\delta}_{R_k} + \sum_{\alpha=1}^{m} \frac{\partial E}{\partial t_\alpha} \delta t_\alpha$$

where the $\underset{\sim}{\delta}$ vector is an arbitrary vector, and δ is the magnitude thereof.

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